Communications

Mesoporous Polystyrenes *via* Lamellar Block Copolymer Assembly

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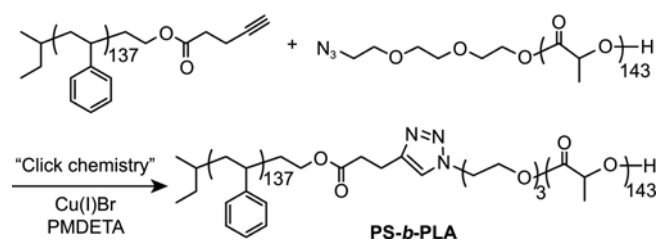*E-mail: chobk@dankook.ac.kr*

Block copolymers (BCPs) are well-known to self-assemble into a variety of nanostructures, such as spherical, cylindrical, gyroid-like, and lamellar morphologies, depending on the volume fraction of the block and/or the chain architecture.[1] Organic mesoporous materials applicable to separations, sensors, *etc.*, could be one of the interesting fields using block copolymers.[2] To prepare organic mesoporous materials, block copolymers should consist of chemically inert and labile blocks. A polystyrene-*block*-polylactide (PS-*b*-PLA) system is a representative example.[3] The PS block is mechanically and chemically robust, while the PLA block is easily hydrolyzed under basic conditions. In a given morphology, PLA domain structures determine the resulting pore morphology. Among possible pore architectures, one-dimensional cylindrical pores have been intensively studied, perhaps because the morphology exists over a wide range of volume fraction, and also because it consists of confined pores.[3,4] Recently, a three-dimensionally connected mesoporous structure from a gyroid morphology was also reported.[5]

On the other hand, due to its wide volume fraction range near 0.5, a lamellar morphology can be obtained as readily as a cylindrical morphology. Nevertheless, a lamellar morphology has rarely been utilized for preparing organic mesoporous materials.[6] With this in mind, it would be interesting to prepare lamellar mesoporous materials using a lamellar BCP. In this paper, we report a mesoporous material, consisting of PS layers, by a chemical etching of sacrificial PLA layers in a lamellar structure.

To obtain the porous material, we first synthesized a block copolymer (PS-*b*-PLA) using a click reaction of individually prepared PS and PLA blocks. The PS was prepared by the anionic polymerization of styrene. The PS end was functionalized with a hydroxyl group, which was converted into an alkynyl group for the next click coupling (Scheme S1(b)). From the ^{1}H NMR data, the number average molecular weight (M_n) of the obtained PS was determined to be 14,400 g/mol. The other PLA block was synthesized by a ring opening polymerization (ROP) of D,L-lactide using triethyl aluminum as the catalyst (Scheme S1(c)). For the click coupling with the PS block, the ROP initiator contained an azide end.[7] From the ^{1}H NMR analysis, the M_n was estimated to be 10,500 g/mol, and the GPC data showed the polydispersity (M_w/M_n) to be 1.06. The click coupling was carried out using Cu(I)Br/PMDETA as the catalyst (Scheme 1).[8] The obtained block copolymer showed a triazolyl hydrogen at 7.39 ppm in the ^{1}H NMR spectrum (Figure S1), and the polydispersity was 1.04, indicative of its narrow molecular weight distribution (Figure S2). The volume fraction (f) of the PS block was calculated to be 0.60.

The differential scanning calorimetry (DSC) data of the block copolymer displayed two glass transitions at 51.4 °C
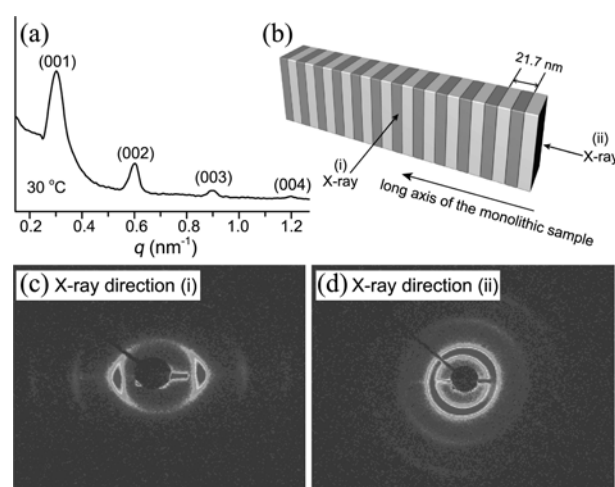
Figure 1. (a) SAXS data at 30 °C, (b) schematic representation of the oriented lamellar sample, and (c,d) two-dimensional SAXS data of the oriented lamellar structure.

Scheme 1. Synthesis of a diblock copolymer (PS-*b*-PLA) *via* "click chemistry".
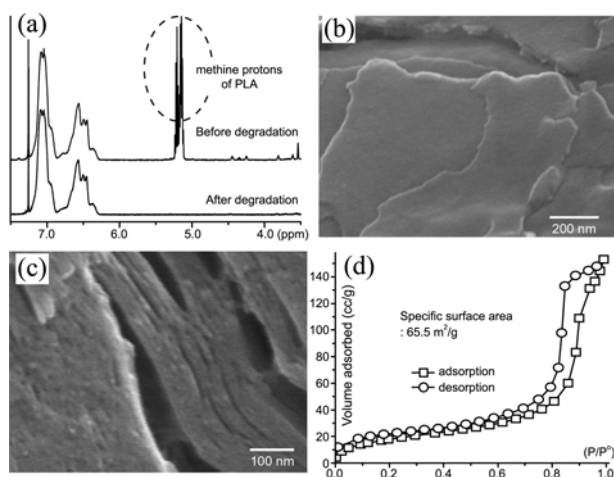
Figure 2. (a) ^{1}H NMR spectra before and after PLA degradation, (b,c) SEM images, and (d) nitrogen adsorption/desorption curve of the porous lamellar material.

and 92.5 °C, which were attributed to the PLA and PS blocks, respectively (Figure S3). The block copolymer showed an ordered morphology, which persisted up to an experimentally accessible temperature of 200 °C. The small angle X-ray scattering (SAXS) data at 30 °C exhibited multiple reflections with *q*-spacing ratios of 1:2:3:4, which indicates a lamellar structure (Figure 1(a)). From the primary reflection, the periodic layer thickness was estimated to be 21.1 nm (Figure 1(b)).

The lamellar morphology could be macroscopically oriented through channel die experiments.[9] The polymer sample was compressed at 135 °C, and annealed for 20 min, then cooled to 50 °C. The obtained sample was monolithic in nature. When the X-ray beam was perpendicular to the long axis of the sample, a spotty reflection pattern was obtained (Figure 1(c)). On the other hand, when the X-ray beam was paralleled to the long axis of the sample, a ring-type pattern was observed (Figure 1(d)). The beam direction-dependent X-ray results indicate that the lamellar plane is aligned perpendicular to the long axis of the sample (Figure 1(b)).

The PLA block in the lamellar morphology could be degraded in 0.5 M NaOH solution. In the ^{1}H NMR spectrum after the degradation, the methine protons of the PLA block disappeared, which is indicative of the complete removal of the PLA block (Figure 2(a)). Furthermore, the elution volume of the degraded polymer in the GPC moved to that of the PS precursor (Figure S4).

The porous PS layers were confirmed by scanning electron microscopy (SEM). Large lamellar plates with smooth surfaces were observed in the SEM image viewed from the direction perpendicular to the lamellar plane (Figure 2(b)). Additionally, the SEM image viewed from the direction parallel to the lamellar plane showed porous regions in between stacked PS layers (Figure 2(c)). The SAXS data displayed two broad lamellar reflections with the primary *d*-spacing of 21.7 nm (Figure S5). This indicates that the average lamellar dimension do not change even after the

degradation. However, the broader peak width suggests that lamellar pores have a wide size distribution.

To better understand the porous structure, we measured nitrogen adsorption/desorption isotherms of the porous PS (Figure 2(d)). The isotherm curve is type IV, which is the type that is observed in mesoporous materials. The hysteresis loop is different from the H1 or H2 type found in conventional cylindrical porous materials.[10] Instead, the hysteresis fitted the H4 type from the mesoporous materials, consisting of slit-like (lamellar) pores.[11] Using the Brunauer-Emmett-Teller (BET) method, the specific surface area of the lamellar mesoporous materials was determined to be 65.5 m^2/g.

It should be noted that no lamellar mesoporous silica has been reported to date. That might be due to the calcinations process at high temperatures (near 500 °C), which results in the collapse of the lamellar silica.[12] In contrast, the organic porous lamellar sample in this study can be prepared in a mild etching condition. This might produce the lamellar mesoporous PS material.

In summary, we synthesized a PS-*b*-PLA block copolymer by a click coupling of individually prepared PS and PLA blocks. The block copolymer self-assembled into a lamellar morphology. Using a channel die technique, the lamellar plane was oriented perpendicular to the long axis of the sample. A chemical etching of the PLA block produced a lamellar mesoporous PS material.

References

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