

Solid-State NMR Study on the Structure and Dynamics of Triblock Copolymer P123 Remaining in SBA-15 after Solvent Washing

Oc Hee Han* and Yoon Kyung Bae^a

Analysis Research Division, Daegu Center, Korea Basic Science Institute, Daegu 702-701, Korea. *E-mail: ohhan@kbsi.re.kr
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The structures and dynamics of triblock poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) copolymers, which are structure directing agents for various mesoporous materials, have been studied extensively.¹⁻⁸ The structures and dynamics of this neutral block-copolymer-type surfactant in both as-synthesized mesoporous materials and micelles were regarded as helping to explain the formation of these mesoscopic structures.⁸⁻¹¹ In the triblock copolymers, poly(propylene oxide) (PPO) block is hydrophobic while poly(ethylene oxide) (PEO) block is hydrophilic. Therefore, above a critical micelle concentration and temperature, micelles consisting of core and corona regions mainly made of PPO and PEO blocks, respectively, are produced.¹⁻⁴ The interaction of PEO block in corona regions with inorganic sources such as tetraethyl orthosilicate (TEOS) is strongly related with the microscopic structures in mesoporous materials.⁸⁻¹¹

Before surface functionalization of mesoporous materials, triblock copolymers used as templates are removed by various methods including thermal treatment or washing with solvents.⁹⁻¹³ Compared to thermal treatment, washing is reported to distort the framework of mesoporous materials much less severely.¹¹⁻¹³ However, washing does not easily allow complete removal of organic templates.

In this work, the structures and dynamics of triblock copolymer Pluronic P123 (EO₂₀-PO₇₀-EO₂₀) in SBA-15 were studied, before and after solvent washing, by ¹³C single pulse (SP)-magic angle spinning (MAS) and cross polarization (CP)-MAS nuclear magnetic resonance (NMR) spectroscopy. The study results revealed the interaction of organic triblock copolymer and inorganic mesoporous materials, as well as the interaction of various solvents with the copolymers in mesopores. Although ¹H MAS NMR was reported to be much more sensitive in ascertaining the complete removal of structure directing reagents from as-synthesized mesoporous materials,¹³ ¹³C SP-MAS and CP-MAS NMR are better techniques to study the structures and dynamics of triblock copolymers remaining in mesoporous materials.

As reported previously,¹¹ SBA-15 was synthesized with Pluronic P123 (poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol); Mn ~ 5800; Aldrich, U.S.A.) triblock copolymer as a structure directing agent and TEOS (Aldrich, U.S.A.) as a silica source. In a typical

synthesis, 4 g (0.69 mmol) of P123 was dissolved in 30 g of water and 120 g of 2 M HCl solution and then stirred at 35 °C for an hour. Then, 8.5 g (40.8 mmol) of TEOS was added dropwise into the homogeneous solution while stirring at 35 °C for 20 h. The obtained gel was aged at 100 °C without stirring for 24 h. The solid white product, which was denoted as SBA-15-as-syn, was filtered, washed with distilled water and air-dried at room temperature. Solvent washed samples were prepared by rinsing 0.5 g of SBA-15-as-syn placed on a Büchner funnel with a 20-mL-dose of ethanol or water and repeating this rinsing 4 times. SBA-15 samples washed with water or ethanol were denoted as SBA-15-water-washed and SBA-15-ethanol-washed, respectively. Only 24% of the P123 in SBA-15-as-syn was washed out by water, compared to 74% during ethanol washing. The amounts of depleted P123 were measured by ¹H MAS NMR.¹³

All solid-state NMR spectra were acquired on a DSX-400 spectrometer (Bruker Biospin GmbH, Germany) with a magnetic field strength of 9.4 T and 4 mm rotors at room temperature. ¹³C CP-MAS spectra were acquired with a 3 s pulse sequence repetition delay, a 5 μs proton pulse length (90° flip), a 2 ms contact time, a spectral width of 100 kHz, and a spinning rate of 4.5 kHz. ¹³C SP-MAS spectra under dipolar proton decoupling were obtained with a 30 s pulse sequence repetition delay and a 2 μs carbon pulse length (36° flip). All chemical shifts in ppm were referenced to external tetramethylsilane.

Representative ¹³C CP-MAS and SP-MAS NMR spectra of the SBA-15-as-syn, SBA-15-water-washed, and SBA-15-ethanol-washed samples are shown in Figures 1a, 1b, and 1c, respectively. Our ¹³C SP-MAS spectra of SBA-15-water-washed indicated that the water washing process disturbed the overall molecular ordering of P123, which was manifested as broadened linewidths compared to those of SBA-15-as-syn. However, the linewidth of the PEO block peak was significantly wider in the CP-MAS spectrum than in the corresponding SP-MAS spectrum. Signals in MAS spectra reflect the relative carbon populations for individual peaks while CP tends to enhance the signal from the rigid state. The drastically widened peak for the PEO blocks in the CP-MAS spectra must have been mainly due to the rigid PEO carbons with a wide structural distribution while all of the PEO block, both the rigid and the relatively mobile, induced the corresponding peak in the MAS spectra. The results suggest that the PEO block carbons are forced to exist in two significantly different motional states, rigid and mobile, after

^aPresent address: School of Advanced Materials Science & Engineering, Sungkyunkwan University, Suwon 440-746, Korea

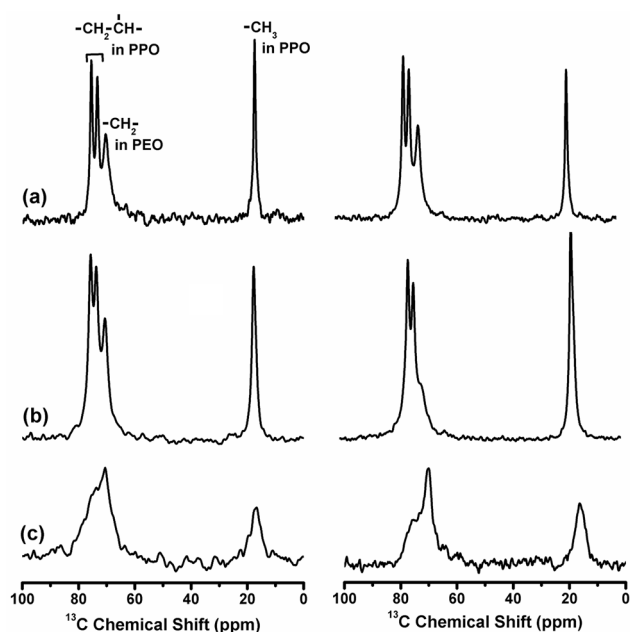


Figure 1. Representative ^{13}C SP-MAS (left column) and CP-MAS (right column) NMR spectra of SBA-15-as-syn (a), SBA-15-water-washed (b), and SBA-15-ethanol-washed (c). The spectra intensities were not normalized.

the water washing process. The PEO blocks weakly bound to mesoporous materials must have been loosened by water washing. This dramatic motional change of the PEO block compared to the PPO block indicates that the hydrophilic PEO blocks were relatively more influenced by water washing.

The peaks in the MAS spectra of SBA-15-ethanol-washed were featureless and much wider than those of SBA-15-as-syn. These widened and featureless peaks suggested that the wide structural distribution and reduced motion of both PEO and PO blocks of the remaining P123 caused a chemical shift distribution. If P123 had a relatively fast motion, the signals would be sharp even with structural distribution. The small amount of P123 remaining in SBA-15-ethanol-washed must have adhered on the SBA-15 surface rather than maintaining the micelle structure. The slightly stronger intensity for the PEO block in the CP-MAS spectra than in the MAS spectra of SBA-15-ethanol-washed implied that some of the PEO blocks are more rigid than other carbons of the P123 in SBA-15-ethanol-washed. Stronger adhesion of some PEO blocks to inorganic materials was expected due to hydrophilic properties of both the PEO block and the mesoporous materials surface. Overall the more efficient removal of P123 by ethanol and the greater structural perturbation of the remaining P123 indicated that the presence of both hydrophobic ethyl groups and hydrophilic hydroxyl groups of ethanol allows the ethanol penetrate amphiphilic P123 in SBA-15 much better than water does.

The ^{13}C CP-MAS spectrum of the SBA-15-water-washed sample which was further aged for a month after water washing was almost the same as that of SBA-15-as-syn, as shown in Figure 2, indicating that the P123 remaining in SBA-15-water-washed had been rearranged during one

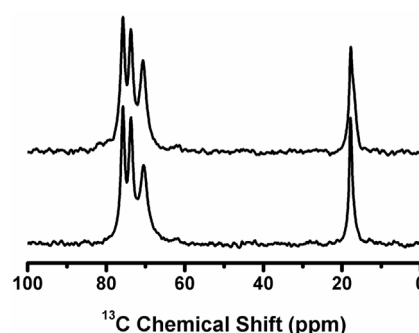


Figure 2. Comparison of the ^{13}C CP-MAS NMR spectrum of the SBA-15-water-washed sample which had been aged for a month after water washing (top) with that of SBA-15-as-syn (bottom).

month. This observation can be explained by the following model: the PEO blocks dispatched from the micropores and in fast motion are re-occluded to the micropores of the silica surfaces during the rearrangement. The perturbed molecular ordering of P123 due to water washing must be in a *meta* stable state and less stable than the ordered structure of the P123 in SBA-15-as-syn.

In summary, our results demonstrated that information on the molecular structures and dynamics of block copolymers in mesoporous materials can be obtained even with simple experiments such as ^{13}C SP-MAS and CP-MAS NMR spectroscopy. PEO blocks interact more intensively with silica mesoporous materials than PPO blocks do, suggesting the presence of hydrophobic PPO core and hydrophilic PEO corona regions, as previously reported.^{8,10,11} In addition, our results confirm that amphiphilic solvents are superior to hydrophilic or hydrophobic solvents for the removal of surfactants from as-synthesized mesoporous materials.

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