Supporting Information

Using Block Copolymer Self-Assembly to Imprint the Crystallization of Polymer Dendrites

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Experimental Section

Size exclusion chromatography (SEC) and Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-ToF MS). Size exclusion chromatographic analysis (SEC) of PS-*b*-PEO was performed at a flow rate of 1 mL/min in methylene chloride at 25 °C and compared with the results of PS (M_n = 29.0 kg/mol) and PEO (M_n = 5.0 kg/mol).[1,2] The peak of PS-*b*-PEO showed a very weak low molecular mass tail around the PEO peak in the SEC chromatogram although any clear bimodal peak was not observed. (Figure S1.) Due to the uncertainty of the SEC chromatogram, it is not certain that the tail is assigned to PEO homopolymer and the isolation of PEO homopolymer from block copolymer was not completely achieved.[1,3] Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-ToF MS) spectrum of PS-*b*-PEO was taken as shown in Figure S2 because it is able to detect small quantities of polymeric products that are not detected by proton and carbon-13 nuclear magnetic resonance spectroscopy (^{1}H and ^{13}C NMR).[4-6] The measurements were performed on a Bruker Daltonics (Billerica, MA) REFLEX II instrument in reflectron mode with a 337 nm wavelength nitrogen laser (3 nm pulse width) and an accelerating voltage of 20 kV. 1,8,9-trihydroxyanthracene (dithranol) was used as matrix for PS-*b*-PEO diblock copolymer with sodium trifluoroacetate as cationizing agent. PS-*b*-PEO was dissolved in tetrahydrofuran (THF) (10 mg/mL) and mixed with matrix (20 mg/mL in THF) and salt (10 mg/mL in THF). The mixing ratio of matrix: cationizing salt: polymer was 10:1:2. One mL of this mixture was spotted onto the target and allowed to dry completely before the measurement. The mass scale was calibrated externally using polystyrene standards. In addition to the peaks around the molecular weight of PS-*b*-PEO (M_n = 25.4 kg/mol), we observed extra spectra around mass (m/z) of 5300. As seen in the inset, the magnification of spectra appear as a series of groups of triplet peaks, each group being made of a large peak (m) and two small peaks appearing at mass numbers of (m +16) and (m+27). The distance between the individual peaks, i.e. the corresponding two small peaks as well as large peak in each group, is +44 Da. It indicates that each of these peaks represents masses that differ by one ethylene oxide group which is monomer unit of PEO.[7,8] The major peak labeled as 5268 is expected to be made up of repeating EO groups (m = 44), one sodium ion (m = 23) and two end groups.

The polymerization of styrene in benzene is initiated by *sec*-butylithium and followed by ω-end-group functionalization with ethylene oxide to form the corresponding polymeric lithium alkoxide (PSOLi). However, only initiation, but no propagation, for ethylene oxide has been observed under conventional reaction conditions.[1] The unreactivity of the chain ends was attributed to the high degree of aggregation of lithium alkoxides, even in a polar medium, and the strength of the association.[9,10] Instead, PS-*b*-PEO synthesis utilizes a polymeric potassium derivative initiator for ethylene oxide polymerization in the presence of dimethylsulfoxide (DMSO). The strength of aggregates decreases with decreasing charge density (increasing size) of the counterion, i.e. in the row, Li^+, Na^+, K^+, Rb^+ and Cs^+.[2] It was reported that the potassium alkoxide additive can initiate ethylene oxide polymerization and form PEO homopolymer in competition with block copolymer formation.[1] As observed by SEC and MALDI-ToF, the diblock copolymer product includes varying amounts of PEO homopolymer that can be minimized by the type of potassium derivative, although it does not contain any detectable amount of PS homopolymer. The removal of this PEO homopolymer may be accomplished by fractional precipitation or column chromatography.[11] But, it is clear that the PS-*b*-PEO with narrow molecular mass distribution contains a shade of PEO homopolymer with lower molecular mass than that of the PEO block. In this paper, we purposely used the PS-*b*-PEO without further purification to study template-directed crystallization. The homopolymer was also systematically added to the PS-*b*-PEO solution to investigate the crystallization behavior with the polymer composition, but will be discussed later. In addition to the presence of potassium additive, some other side reaction must be occurring in this synthesis, such as possible chain transfer between the growing polymeric alkoxide and DMSO. PEO homopolymer and those side products are responsible for the identities of triple peaks observed in MALDI-ToF but the effort for the clarification is beyond the scope of this report.

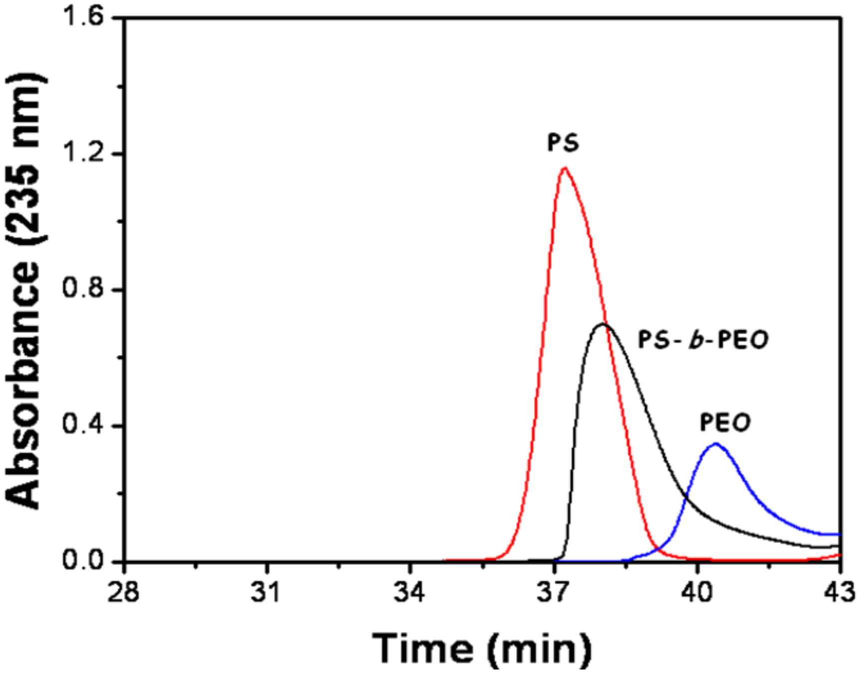


Figure S1. Size exclusion chromatography (SEC) measurements performed in methylene chloride with a flow rate of 1 mL/min using toluene as internal standard. A UV-Vis photodiode array (Waters 2996) was used to record the absorbance spectrum (200 to 800) nm as a function of time.

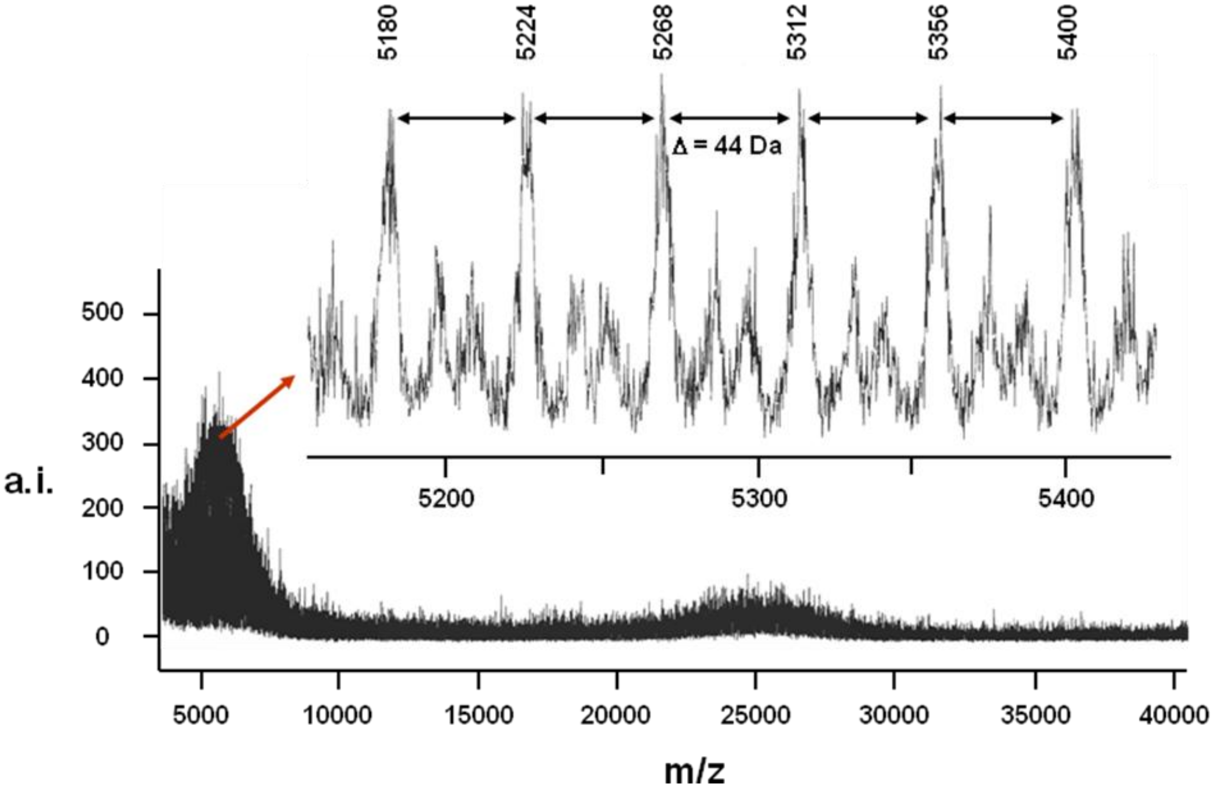


Figure S2. Matrix-assisted laser desorption/ionization time-of-flight mass spectrum (MALDI ToF MS) of PS-*b*-PEO diblock copolymer. The spectrum was measured using dithranol as a matrix and sodium trifluoroacetate as cationizing agent. The inset is magnification of MALDI ToF MS of the peak around mass (m/z) of 5300.

SUPPORTING INFORMATION REFERENCES

(1) Quirk, R. P.; Kim, J.; Kausch, C.; Chun, M. S. *Polym. Int.* 1996, *39*, 3.

(2) Schmalz, H.; Lanzendorfer, M. G.; Abetz, V.; Muller, A. H. E. *Macrom. Chem. Phys.* 2003, *204*, 1056.

(3) Zhu, L.; Cheng, S. Z. D.; Calhoun, B. H.; Ge, Q.; Quirk, R. P.; Thomas, E. L.; Hsiao, B. S.; Yeh, F.; Lotz, B. *Polymer* 2001, *42*, 5829.

(4) Quirk, R. P.; Mathers, R. T.; Wesdemiotis, C.; Arnould, M. A. *Macromolecules* 2002, *35*, 2912.

(5) Polce, M. J.; Klein, D. J.; Harris, F. W.; Modarelli, D. A.; Wesdemiotis, C. *Anal. Chem.* 2001, *73*, 1948.

(6) Nielen, M. W. F. *Mass Spec. Rev.* 1999, *18*, 309.

(7) Lee, H.; Lee, W.; Chang, T.; Choi, S.; Lee, D.; Ji, H.; Nonidez, W. K.; Mays, J. W. *Macromolecules* 1999, *32*, 4143.

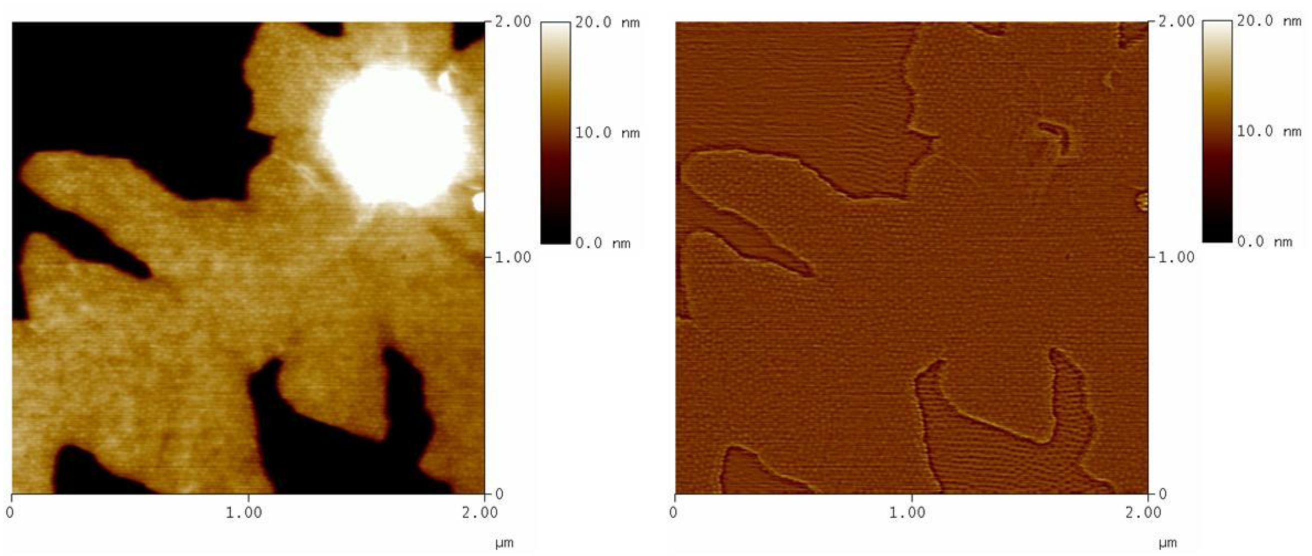
(8) Van Renterghem, L. M.; Feng, X. S.; Taton, D.; Gnanou, Y.; Du Prez, F. E. *Macromolecules* 2005, *38*, 10609.

(9) Halaska, V.; Lochmann, L.; Lim, D. *Coll. Czech. Chem. Comm.* 1968, *33*, 3245.

(10) Hartwell, G. E.; Brown, T. L. *Inorg. Chem.* 1966, *5,* 1257.

(11) Quirk, R. P.; Kim, J.; Rodrigues, K.; Mattice, W. L. *Makrom. Chem., Macromol. Symp.* 1991, *42-3*, 463.

Images Relating to the Results and Discussion Section



(a)

(b)

Figure S3. (a) Height image corresponding to the phase image in Figure 5 and (b) after processed with high pass filter function for better resolution.