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Synthesis and Characterization of Helix-Coil Diblock Copolymers with Controlled Supramolecular Architectures in Aqueous Solution

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Materials

Monodispersed poly (ethylene glycol) monomethyl ether with different molar masses ranging from 1100 to 5000 g/mol was commercial reagents from Fluka company. They were purified by dissolving in a mixture of chloroform and THF and precipitating in absolute ethyl ether to remove the higher molecular grades. Anisole were refluxed over CaH_2 and distilled out just before use. Dichloromethane was dried over anhydrous calcium chloride. N, N, N', N', N"-pentamethyldiethylenetriamine (PMDETA) (98%) were obtained from TCI. HPLC grade dioxane, 4-N, N-dimethylamino-pyridine (DMAP, 99%), 2-bromoisobutyryl (98%) were purchased from Acros. Unless specified, all other reagents were used as obtained without further purification.

Instrumentation

All ^1H NMR spectra were measured on a Bruker ARX 400 spectrometer at room temperature. The polydispersities of the PEO macroinitiators and the diblock copolymers were determined by gel permeation chromatography (GPC) using a set of Waters Styragel columns HT2+HT3+HT4 and Waters 2410 refractive index detector, with THF as the eluent at a flow rate of 1.0 ml/min at 35 ℃. The system was calibrated with polystyrene standard. Circular dichroism spectra were recorded on JASCO J-810 CD spectrophotometer using 1 cm quartz cell. Optical rotations were measured at 365 nm wavelength with JASCO polarimeter P-1030.

Synthesis of the macroinitiator

The macroinitiators were obtained by the esterification of PEO with 2-bromoisobutyryl bromide. The following procedure took PEO with the molecular weight of 2000 as an example**.** A mixture of fractionated PEO (M_w=2000, DPI=1.02) (18.6 g, 10.0 mmol), DMAP (1.22 g, 10.0 mmol), and triethylamine (2.02 g, 20.0 mmol) was dissolved in dichloromethane. After cooling in an ice bath, 2-bromoisobutyryl (5.73 g, 25.0 mmol) in dichloromethane was added dropwise. The solution was stirred overnight at room temperature. The crude product obtained after evaporation of the solvent was recrystallized several times from absolute ethanol and absolute ethyl ether. The resultant white powder was dried under vacuum.

Synthesis of poly{(+)-2,5-bis[4'-((s)-2-methylbutoxy)phenyl]styrene}-*b*-Poly(ethylene oxide)

The monomer, (+)-2,5-Bis[4'-((s)-2-methyl butoxy)phenyl]styrene (MBPS), was prepared as described in a previous paper.[1] The block copolymers were synthesized via atom transfer radical polymerization with the initiating system of the macroinitiator / CuBr / PMDETA. For example, a solution of PMDETA (0.0035 g, 0.02 mmol) in anisole (0.2 ml) was added to the mixture of the PEO (M_w=2000) macroinitiator (0.040 g, 0.02 mmol), CuBr (0.0029 g, 0.02 mmol) and MBPS (0.43 g, 1 mmol). After being degassed with three freeze-thaw cycles, the tube was sealed off under vacuum. The polymerization was carried out at 90 ℃ for several hours. The reaction solution was diluted with THF, filtered over alumina for the removal of copper

(II), and precipitated from methanol. To remove the monomer, the crude products were further puried by repeatedly dissolving in THF and precipitating in methanol for three times, and finally the white products were dried under vacuum.

Preparation of micellar solution

The diblock copolymers PEO-*b*-PMBPS were dissolved in dioxane to give different copolymer solution with varying concentrations (0.01-1.0 wt.-%). Deionized water was added to the solutions at a rate of 0.5wt.-% every 15 s with vigorous stirring. After the water contents reached 35 wt.-%, the solutions were dialyzed against water for 3 days to remove dioxane.

Sample preparation of transmission electron microscopy

Transmission Electron Microscopy (TEM) was performed on a JEM-100CX TEM operating at an acceleration voltage of 100 kV. The copper grids were precoated with a thin film of Formvar and then coated with carbon. The solutions were deposited onto copper EM grids in air for several minutes. Excess solutions were blotted away with a strip of filter paper.

References

[1] Z. N. Yu, X. H. Wan, H. L. Zhang, X. F. Chen, Q. F. Zhou, *Chem. Commun.* **2003**, *8*, 974.

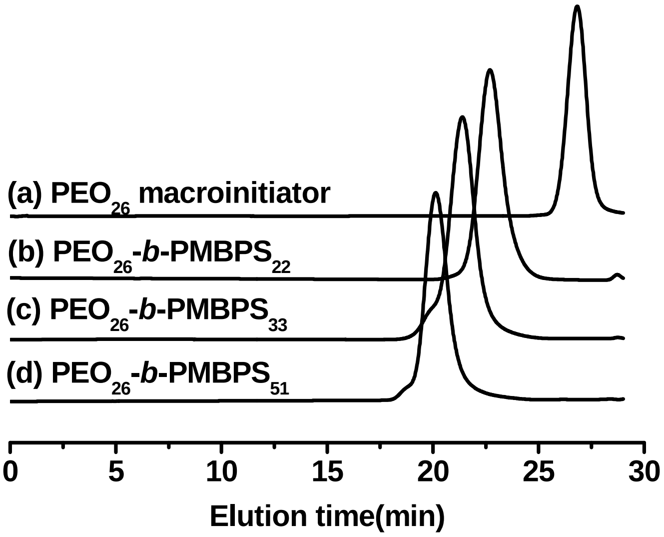

Figure S1. GPC curves of the macroinitiator PEO$_{26}$ (a), and the diblock copolymers PEO$_{26}$-*b*-PMBPS$_{22}$ (b), PEO$_{26}$-*b*-PMBPS$_{33}$ (c), and PEO$_{26}$-*b*-PMBPS$_{51}$ (d).

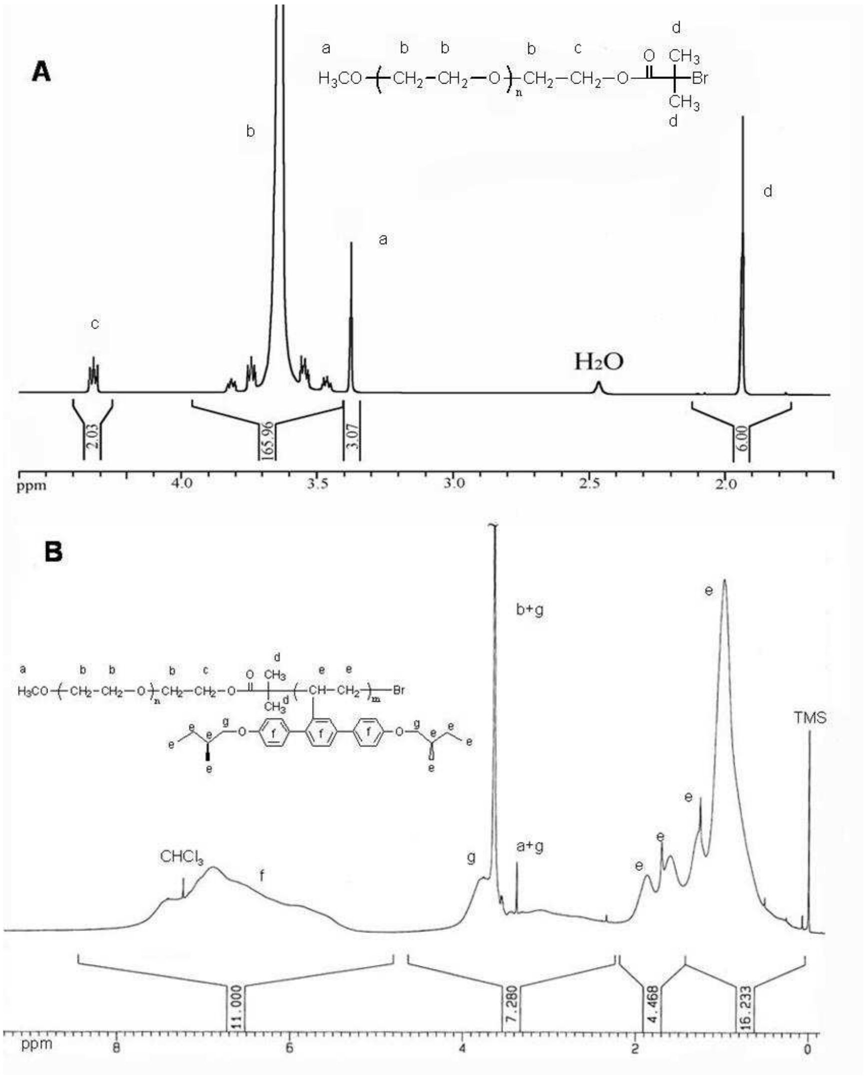

Figure S2. ^{1}H NMR spectra of the macroinitiator PEO-Br (M_w=2000)(A) and PEO_{26}-*b*-$PMBPS_{33}$ (B) in $CDCl_3$.