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A novel approach to prepare polymer mixed-brushes *via* single crystal surface patterning

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Experimental

Materials

Polyethylene glycol monomethyl ether 5000 (PEG) (Aldrich) was dried before use by removing residual water by azeotropic distillation with toluene (Merck, > 99%) on a water separator. 4-(Dimethylamino) pyridine (DMAP, Merck) and 2,2′-bipyridine(bipy, Merck, 98%) were used as received without purification. Methylene dichloride (CH_2Cl_2, Merck, > 99.5%) was shaken with concentrated H_2SO_4 (Merck, 95-97%) until the acid layer remained colorless, then washed with water, and finally distilled with CaH_2 (Merck, ~ 95%). 2-Bromoisobutyryl bromide (Merck) was distilled under vacuum. Triethylamine (TEA, Merck, > 99%) was stored with CaH_2 over night, and then distilled. Inhibitors in styrene (St, Merck, > 99%) and methyl methacrylate (MMA, Merck, > 99%) were removed by passing the monomers over an alumina column, and then distilled under reduced pressure. CuBr (Alfa Aesar, 98%) and CuCl (Merck, ≥ 97%) were purified by stirring with glacial acetic acid (Merck, > 99.8%), filtered and washed three times with ethanol (Merck, 99.5%) and twice with diethyl ether (Merck, > 99%), and finally dried under vacuum. Chlorobenzene (CB, Merck, > 99%) was washed with concentrated H_2SO_4 to remove thiophenes, and then distilled over anhydrous calcium chloride (Merck). All other reagents were purchased from commercial sources and used as received without purification.

Methods

The bromo-capped (PEG) macroinitiator (PEG-Br) was synthesized according to the literature [1]. In an experiment a 7.50 mmol DMAP in 10 mL dried methylene dichloride was mixed with 5.00 mmol TEA. The solution was transferred into a 250 mL three-neck round-bottom flask equipped with a reflux condenser, dropping funnel, gas inlet/outlet, and a magnetic stirrer. After cooling to 0 °C, a solution of 12.50 mmol 2-bromoisobutyryl bromide in 10 mL CH_2Cl_2 was added under stirring. Then a solution of 5 mmol PEO in 50 mL dried CH_2Cl_2 was added dropwise into flask slowly in 1 h, and a yellow dispersion was formed. Subsequently, the temperature was increased to room temperature. The reaction was let proceed under stirring for 18 h. Finally, the crude product was filtered, precipitated with cold diethyl ether, recrystallized from ethanol, washed with cold diethyl ether and dried under vacuum at room temperature [1,2]. The diblock copolymers of PEG-*b*-PS and PEG-*b*-PMMA including various molecular weights of PS and PMMA blocks were synthesized via solution polymerization in chlorobenzene by normal atom transfer radical polymerization (ATRP).

In a typical batch, a glass reactor with two vacuum valves, in order to purge with pure nitrogen, and an inlet in its uppermost part to charge and discharge the materials, was filled with appropriate ratio of monomer, PEG-Br macroinitiator, catalyst (CuBr and CuCl for St and MMA polymerization, respectively), bipy as a ligand and chlorobenzene as solvent $(([St]_0/[MI]_0/[CuBr]_0/[bipy]_0/[CB]_0)=240/1/1/3/66)$ and $(([MMA]_0/[MI]_0/[CuCl]_0[CuCl_2]_0/[bipy]_0$

/[CB]$_0$)=177/1/1/0.07/3/375). After purging with high purity nitrogen, for 20 minutes, the valves and inlet were closed, and the reactor was immersed in a thermostatic oil bath at desired temperature (110 and 65°C for St and MMA polymerization, respectively). Due to higher reactivity of MMA in comparison with St [3,4], $CuCl_2$ was used as deactivator for better controlling of polymerization [5]. The system was usually stirred to ensure better contact of reagents. After passing desired time, the reactor was cooled to room temperature. The reaction mixture was diluted with tetrahydrofuran (THF, Merck, > 99.5%) and then was filtered through a neutral Al_2O_3 (Merck, 70-230 mesh ASTM) column to remove the catalyst, and precipitated with petroleum ether (Merck, >95%). The synthesized diblock copolymers were obtained and dried under vacuum overnight at room temperature. Related explanations of synthesis procedures were described elsewhere [6,7]. (Characteristic of ATRP, the GPC traces (Figure S1) are narrow, symmetric, mono-modal, and move with increasing conversion towards lower elution volume, i.e. elevated molecular weights. The molecular characterization data of diblock copolymers used in this work are reported in Table I.

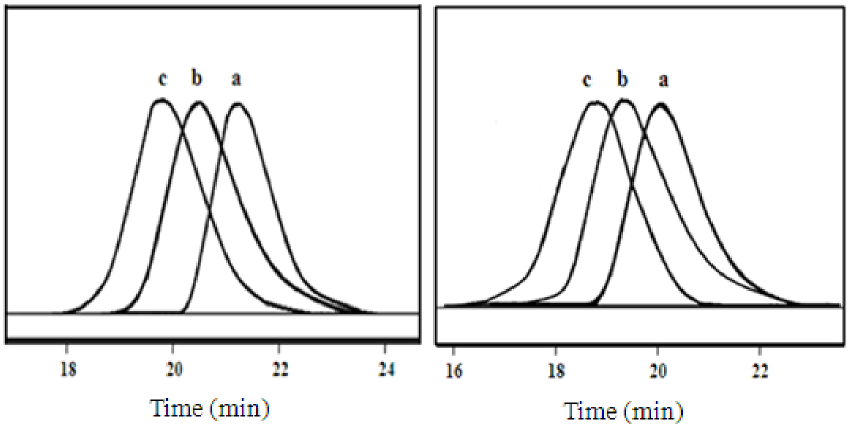

Figure S1. Evolution of GPC traces with polymerization time. (Left) PEG_{5000}-*b*-PS_{4600} (a), PEG_{5000}-*b*-PS_{10000} (b), and PEG_{5000}-*b*-PS_{14800} (c); (Right) PEG_{5000}-*b*-$PMMA_{8700}$ (a), PEG_{5000}-*b*-$PMMA_{13100}$ (b), and PEG_{5000}-*b*-$PMMA_{17100}$ (c).

Apparatus

The chemical structure of block copolymers was confirmed by ^{1}H NMR spectroscopy on a BRUKER (AVANCE DPX) spectrometer at frequency of 400 MHz, which was also used to determine the composition of the copolymers. Deuterated chloroform ($CDCl_3$) was used as a solvent. The polydispersity indexes were determined by GPC on a WATER 1515 (USA) gel permeation chromatography instrument with a set of HT3, HT4, and HT5, μ-styragel columns with DMF and THF as eluents for PS and PMMA respectively (1.0 mL/min) at 35 °C. A set of monodisperse polystyrene standards were utilized for calibration.

Olympus PMG3optical microscope was mainly used to take a first look on the single crystals population distribution and the sample uniformity. For optical microscopy, a silicon wafer was used as substrate.

To measure the overall single crystal thickness and identify the surface morphologies by surface stiffness changes and height variances, the single crystal solution was dropped onto a silicon wafer and quickly dried by a stream of high purity nitrogen and observed under an atomic force microscope (AFM, Nanoscope IIIA). The height and phase images provide insight into the surface topologies of the tethered PS and PMMA chains on the PEG lamellar substrate.

A silicon tip in the tapping mode was utilized. During AFM scanning, the cantilever tip-to-sample force required to be carefully adjusted to avoid damages. For the tip-to-sample force, a large force could lead to tip penetrations into the thin tethered chain layers, and disturb the materials at the layer surfaces. A scan rate of 1 Hz and a resolution of 512 × 512 were selected to take high quality images. Scanning transmission electron microscopy (STEM) experiments were carried out adopting a FEI Quanta 400 operated at 30 kV with a tungsten filament.

In order to measure the glass transition temperature (T_g) and crystallization temperature (T_c) of synthesized diblock copolymers differential scanning calorimetry (DSC) (NETZSCH, F3 Maia200) was utilized.

Single crystal structure and morphology was observed in a transmission electron microscope (TEM, EM 208 Philips) under low doze condition with an accelerating voltage of 100 KeV and filaments of (electron gun) tungsten. Magnification ranges from less than 50× up to 1,200,000×. The selected area electron diffraction (SAED) experiments were also conducted to determine the chain orientation in the copolymer single crystals. Calibration of the SAED spacing values smaller than 0.384 nm was carried out using evaporated thallous chloride, which has the largest first-order spacing diffraction of 0.384 nm. Spacing values larger than 0.384 nm were calibrated by doubling the d-spacing values of the first-order diffractions. A standard copper grid was used as substrate for TEM measurement.

Tables

Table S1. The effect of PS block molecular weight on various parameters of single crystals

Sample	**T (°C)**	**d^{total}_{matrix} (nm)**	**d^{PEG}_{matrix} (nm)**	**d^{PS}_{matrix} (nm)**	**$d^{total}_{dispersed}$ (nm)**	**$d^{PEG}_{dispersed}$ (nm)**	**$d^{PMMA}_{dispersed}$ (nm)**	**σ^{PS} (nm^{-2})**	**σ^{PMMA} (nm^{-2})**	**Height Variance (nm)**	**Domain size (nm)**
PEG_{5000}-*b*-PS_{4600} /PEG_{5000}-*b*-$PMMA_{17100}$	23	14.2	6.8	3.7	12.3	2.7	4.8	0.51	0.20	1.9	302 (0.3%)[a]
PEG_{5000}-*b*-PS_{10000} /PEG_{5000}-*b*-$PMMA_{17100}$	23	16.4	4.9	5.7	12.3	2.7	4.8	0.37	0.20	4.1	295 (0.3%)
PEG_{5000}-*b*-PS_{14800} /PEG_{5000}-*b*-$PMMA_{17100}$	23	18.4	4.0	7.2	12.3	2.7	4.8	0.30	0.20	6.1	286 (0.5%)
PEG_{5000}-*b*-PS_{4600} /PEG_{5000}-*b*-$PMMA_{13100}$	23	14.2	6.8	3.7	11.2	3.0	4.1	0.51	0.22	3.0	324 (0.4%)
PEG_{5000}-*b*-PS_{10000} /PEG_{5000}-*b*-$PMMA_{13100}$	23	16.4	4.9	5.7	11.2	3.0	4.1	0.37	0.22	5.2	316 (0.3%)

[a] Error percentage in comparison to the average domain size

Table S2. The effect of PMMA block molecular weight on various parameters

Sample	T (°C)	d^{total}_{matrix} (nm)	d^{PEG}_{matrix} (nm)	d^{PS}_{matrix} (nm)	$d^{total}_{dispersed}$ (nm)	$d^{PEG}_{dispersed}$ (nm)	$d^{PMMA}_{dispersed}$ (nm)	σ^{PS} (nm^{-2})	σ^{PMMA} (nm^{-2})	Height Variance (nm)	Domain size (nm)
PEG$_{5000}$-*b*-PS$_{4600}$ /PEG$_{5000}$-*b*-PMMA$_{8700}$	23	14.2	6.8	3.7	10.0	3.5	3.2	0.51	0.26	4.2	350 (0.4%)[a]
PEG$_{5000}$-*b*-PS$_{4600}$ /PEG$_{5000}$-*b*-PMMA$_{13100}$	23	14.2	6.8	3.7	11.2	3.0	4.1	0.51	0.22	3.0	324 (0.4%)
PEG$_{5000}$-*b*-PS$_{4600}$ /PEG$_{5000}$-*b*-PMMA$_{17100}$	23	14.2	6.8	3.7	12.3	2.7	4.8	0.51	0.20	1.9	302 (0.3%)
PEG$_{5000}$-*b*-PS$_{10000}$ /PEG$_{5000}$-*b*-PMMA$_{13100}$	23	16.4	4.9	5.7	11.2	3.0	4.1	0.37	0.22	5.2	316 (0.3%)
PEG$_{5000}$-*b*-PS$_{10000}$ /PEG$_{5000}$-*b*-PMMA$_{17100}$	23	16.4	4.9	5.7	12.3	2.7	4.8	0.37	0.20	4.1	295 (0.3%)

[a] Error percentage in comparison to the average domain size

Table S3. The effect of crystallization temperature on various parameters

Sample	T (°C)	d^{total}_{matrix} (nm)	d^{PEG}_{matrix} (nm)	d^{PS}_{matrix} (nm)	$d^{total}_{dispersed}$ (nm)	$d^{PEG}_{dispersed}$ (nm)	$d^{PMMA}_{dispersed}$ (nm)	σ^{PS} (nm^{-2})	σ^{PMMA} (nm^{-2})	Height variance (nm)	Domain size (nm)
PEG$_{5000}$-*b*-PS$_{4600}$ /PEG$_{5000}$-*b*-PMMA$_{8700}$	23	14.2	6.8	3.7	10.0	3.5	3.2	0.51	0.26	4.2	350 (0.4%)[a]
PEG$_{5000}$-*b*-PS$_{4600}$ /PEG$_{5000}$-*b*-PMMA$_{8700}$	28	15.4	7.4	4.0	11.0	3.9	3.5	0.55	0.29	4.4	349 (0.3%)
PEG$_{5000}$-*b*-PS$_{4600}$ /PEG$_{5000}$-*b*-PMMA$_{8700}$	30	16.1	7.7	4.2	11.4	4.0	3.7	0.58	0.30	4.7	348 (0.3%)
PEG$_{5000}$-*b*-PS$_{4600}$ /PEG$_{5000}$-*b*-PMMA$_{8700}$	32	16.8	8.1	4.4	11.9	4.2	3.8	0.60	0.31	4.9	351 (0.4%)
PEG$_{5000}$-*b*-PS$_{4600}$ /PEG$_{5000}$-*b*-PMMA$_{13100}$	23	14.2	6.8	3.7	11.2	3.0	4.1	0.51	0.22	3.0	324 (0.4%)
PEG$_{5000}$-*b*-PS$_{4600}$ /PEG$_{5000}$-*b*-PMMA$_{13100}$	30	16.1	7.7	4.2	12.5	3.4	4.6	0.58	0.25	3.6	323 (0.5%)
PEG$_{5000}$-*b*-PS$_{10000}$ /PEG$_{5000}$-*b*-PMMA$_{13100}$	23	16.4	4.9	5.7	11.2	3.0	4.09	0.37	0.22	5.2	316 (0.3%)
PEG$_{5000}$-*b*-PS$_{10000}$ /PEG$_{5000}$-*b*-PMMA$_{13100}$	30	18.2	5.5	6.4	12.5	3. 4	4.6	0.41	0.25	5.7	314 (0.5%)
PEG$_{5000}$-*b*-PS$_{4600}$ /PEG$_{5000}$-*b*-PMMA$_{17100}$	23	14.2	6.8	3.7	12.3	2.7	4.8	0.51	0.20	1.9	302 (0.3%)
PEG$_{5000}$-*b*-PS$_{4600}$ /PEG$_{5000}$-*b*-PMMA$_{17100}$	30	16.1	7.7	4.2	13.4	2.9	5.2	0.58	0.22	2.7	303 (0.4%)
PEG$_{5000}$-*b*-PS$_{10000}$ /PEG$_{5000}$-*b*-PMMA$_{17100}$	23	16.4	4.9	5.7	12.3	2.7	4.8	0.37	0.20	4.1	295 (0.3%)
PEG$_{5000}$-*b*-PS$_{10000}$ /PEG$_{5000}$-*b*-PMMA$_{17100}$	30	18.2	5.5	6.4	13.4	2.9	5.2	0.41	0.22	4.8	292 (0.5%)
PEG$_{5000}$-*b*-PS$_{14800}$ /PEG$_{5000}$-*b*-PMMA$_{17100}$	23	18.4	4.0	7.2	12.3	2.7	4.8	0.30	0.20	6.1	286 (0.5%)
PEG$_{5000}$-*b*-PS$_{14800}$	30	20.1	4.4	7.8	13.4	2.9	5.2	0.33	0.22	6.7	287

/PEG_{5000}-*b*-$PMMA_{17100}$	(0.4%)

[a] Error percentage in comparison to the average domain size

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