Supporting Information

High Flux CO_2 Transporting Nanochannel Fabricated by Self-Assembly of Linear-Brush Block Copolymer

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Experiment

Materials

Chlorobenzene (Analytical purity, Beijing Chemical Reagents Co.) was treated with powdered CaH_2 and distilled before use. Toluene, THF (Analytical purity, Beijing Chemical Reagents Co.) were distilled from Na/benzophenone under N_2. CuBr was synthesized from $CuBr_2$. Cellulose acetate (CA, Analytical purity, Beijing Chemical Reagents Co.), 7-hydroxyl-4-methylcoumarin (Analytical purity, Beijing Chemical Reagents Co.), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 97%, J&K), 1-(chloromethyl)-4-vinylbenzene (97%, Aldrich), were used as received. Styrene (Analytical purity, Beijing Chemical Reagents Co.) was distilled prior to use. Oligo(ethylene glycol) methyl ether methacrylate (OEGMA, M_n=475, Aldrich) was passed through a basic alumina column to remove inhibitor.

Measurements

The molecular weights (MWs) and molecular weight distributions of all copolymers were measured by gel permeation chromatography (GPC) with a Waters 2410 instrument equipped with three Waters μ-Styragel columns (10^3, 10^4, and 10^5 Å). THF was the mobile phase at the flow rate of 1.0 mL/min at 35 $^{\circ}$C. The calibration curve was obtained by PS standards. The weight fraction of OEGMA block was based on the results from the nuclear magnetic resonance spectroscope (NMR) performed on a Bruker ARX 300MHz spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as the reference.

Thermal analysis of the BCP was carried out in a TA differential scanning calorimeter (DSC) Q100 calorimeter with a heating rate 20 ^{o}C/min and over the temperature range from -90-200 ^{o}C.

FT-IR spectra were recorded at room temperature using a Bio-Rad FT-IR system coupled to a computer. The spectra were collected over the range 600-4000 cm^{-1}.

Small angle X-Ray scattering (SAXS) experiment was carried out on the SAXSess high-flux small-angle X-ray scattering instrument (Anton Paar) equipped with Kratky block-collimation system. The X-ray was generated using a Philips PW3830 sealed-tube X-ray generator with Cu target. The wavelength was 0.1542 nm. The power of the generator used for measurement was 40 kV and 40 mA. The X-ray intensities were recorded on an imaging-plate detection system with a pixel size of 42.3 × 42.3 μm^{2}. The distance from the sample to detector was 264.5 mm and the exposure time was 600 s. The treatment of original experimental data such as data acquisition, background subtraction, data reduction was handled by Anton Paar SAXSquant 1.01 software and PCG software package.

The microphase separation of sample was observed by TEM. 1 % BCP solution in toluene was added onto the TEM grid with a thin layer of carbon, and absorbed most of the solution with filter paper. The thin film was then annealed in benzene vapor for 2 h at room temperature, and dried before TEM observed. To enhance the electron density contrast between the POEGMA and PS phases, the POEGMA domains were stained by RuO_4 vapor at room temperature for 3 min. TEM studies were performed on a Hitachi H-800 electron microscope.

The surface microphase separation structure was confirmed by AFM experiments by using an Agilent AFM series 5500 (Agilent Technologies). Imaging was carried out in the AAC mode. The used cantilevers (Nanosensor) have frequencies within of 204–497 kHz and force constant values 10–130 N/m.

Permeation Measurements

Gases permeation measurements were based on previous works and carried out with a home-built stainless steel permeation apparatus. The pure gases studied were He, N_2 and CO_2. The permeation rate (P) and ideal selectivity (α) of CO_2 over another gas

were calculated.[1]

Synthetic Procedures

Initiators, phenyl 2-bromo-2-methylpropanoate (**1**), prop-2-ynyl 2-bromo-2-methylpropanoate (**2**), were synthesized according to literatures.[2] Synthesis of UV-crosslinkable monomer coumarin-derived styrene (St-C), was synthesized by coupling of coumarin and 1-(chloromethyl)-4-vinylbenzene.[3]

Synthesis of PS-StC-Br 0.387 g initiator **1** (1.59 mmol), 0.266 g CuBr (1.84 mmol), 3.370 g of St-C (11.50 mmol), 60.090 g styrene (0.58 mol), 0.324 g of PMDETA (1.87 mmol) were added into a tube. The mixture was degassed by three freeze-pump-thaw cycles, and sealed under vacuum. The reaction tube was placed in an oil bath at 90 ^{o}C for 6 h. The polymerization was quenched by dipping the tube in ice/water and the tube was broken. The mixture was diluted with CH_2Cl_2, passed through a basic alumina column, and precipitated into methanol. The white powder was filtered and dried in vacuum. The resulting product had MW of 21.0 k, and PDI of 1.17 determined by GPC, and St-C weight fraction was 5% determined by ^{1}H NMR.

Synthesis of PS-StC-N$_3$

The procedure for the transformation of PS-StC-Br into PS-StC-N$_3$ was adapted from the literature.[4] Typically, PS-StC-Br (5.00 g), excessive NaN$_3$ (0.10 g), and DMF (25 mL) were added in a flask. The mixture solution was stirred vigorously at room temperature for 24 hour. The PS-StC-N$_3$ was then precipitated into methanol, filtered, and dried in a vacuum.

Synthesis of Block Copolymer 0.416 g PS-StC-N$_3$ (0.02 mmol) was dissolved in 2.0 g of chlorobenzene. And then 4.0 mg initiator **2** (0.02 mmol), 0.531 g of OEGMA (2.07 mmol), 2.8 mg of CuBr (0.02 mmol), 10 μL of HMTETA (0.04 mmol) were added. The mixture was degassed by three freeze-pump-thaw cycles, and sealed under vacuum. The reaction tube was placed in an oil bath at 90 ^{o}C for 20 h. The polymerization was quenched by dipping the tube in ice/water and the tube was broken. The mixture was diluted with CH_2Cl_2, passed through a basic alumina column, precipitated into cold petrol ether, and washed with water to remove POEGMA

homopolymer. The block copolymers were filtered and dried in vacuum. The resulting product had MW of 28.9 k, and PDI of 1.17 determined by GPC, and POEGMA blocks weight fraction was 39.2% determined by ^{1}H NMR.

Membrane Fabrication

On silicon wafer, CA sacrifice layer was made by spin-coating 4 wt% acetone solution at 1000 rpm. Then the BCP film was made by spin-coating at 1000 rpm with 4% toluene solutions onto CA film. The film was annealed in benzene vapor for 2 h at room temperature, dried at N_2 atmosphere over night, and then in vacuum at temperature elevated gradually from ambient temperate to 80 ^{o}C. After that, the BCP film was crosslinked by exposure on UV light (λ=365 nm) for 5 min. At last, CA was dissolved by acetone, and free standing film was obtained. The average thickness of the film was determined by cross section view from scanning electron microscope (SEM).
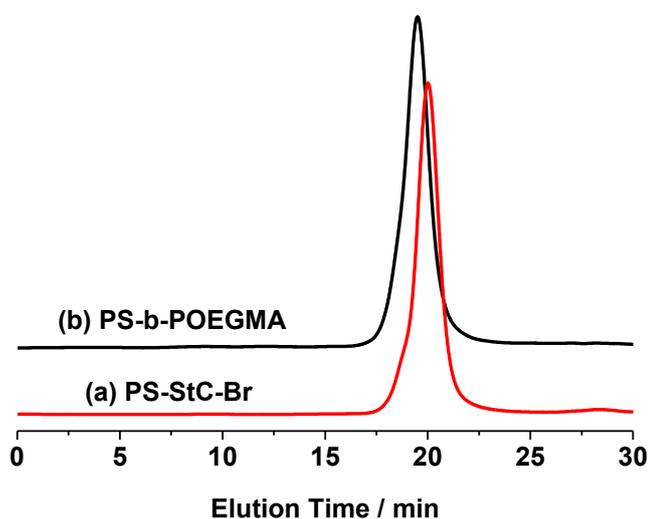
Figure S1. GPC curves of PS-StC-Br macrointiator (a) and PS-*b*-POEGMA (b), indicating well-controlled polymerization of BCP.
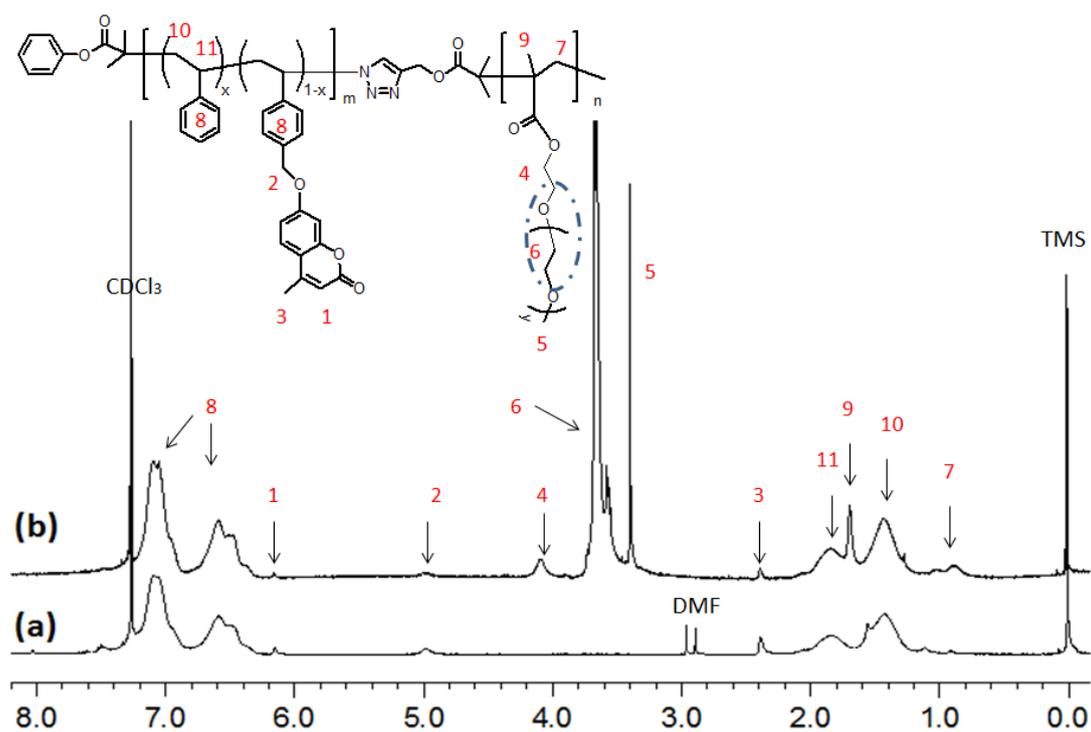
Figure S2. ^{1}H NMR spectrum of PS-StC-N$_3$ (a) and BCP (b) in CDCl$_3$ (300 MHz).
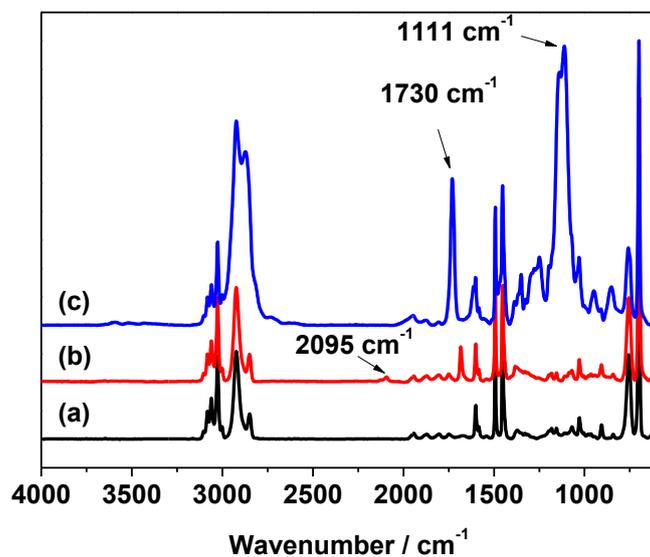
Figure S3. FTIR spectrum of PS-StC-Br (a) and PS-StC-N$_3$ (b) and PS-b-POEGMA (c).
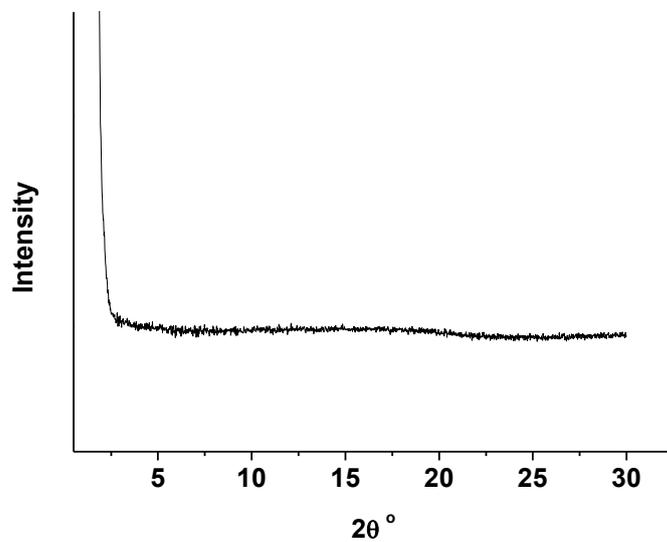
Figure S4. Wide angle X-ray scattering of POEGMA homopolymer at room
temperature (M_n=19.0 k, PDI=1.15)
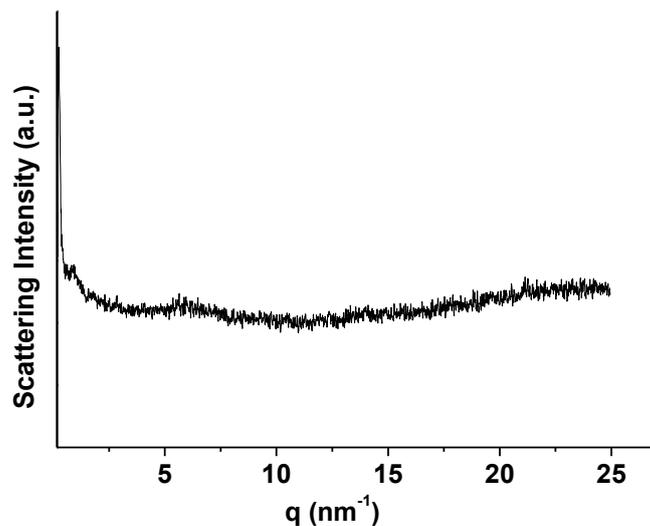
Figure S5. Wide angle X-ray scattering of BCP at room temperature (obtained from
the SAXSess instrument at wide angle part).

Table S1. Permeances of gases across polymer film.

P/psi[a]	T/°C[b]	CO_2[c]	He[c]	N_2[c]	CO_2/He[d]	CO_2/N_2[d]
2	-15	12400	11100	5500	1.1	2.3

2	20	47400	22700	8400	2.1	5.6
2	45	78900	33700	10000	2.3	7.9
3	20	78600	41600	16200	1.9	4.8

[a] upstream pressure; [b] experiment temperature; [c] average permeances of gases, obtained from 6 independent measurements (10^{-6} $cm^3 \cdot cm^{-2} \cdot s^{-1} \cdot cmHg^{-1}$); [d] the pure gas selectivity.

References

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