Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Highly Conductive Side Chain Block Copolymer Anion Exchange Membranes

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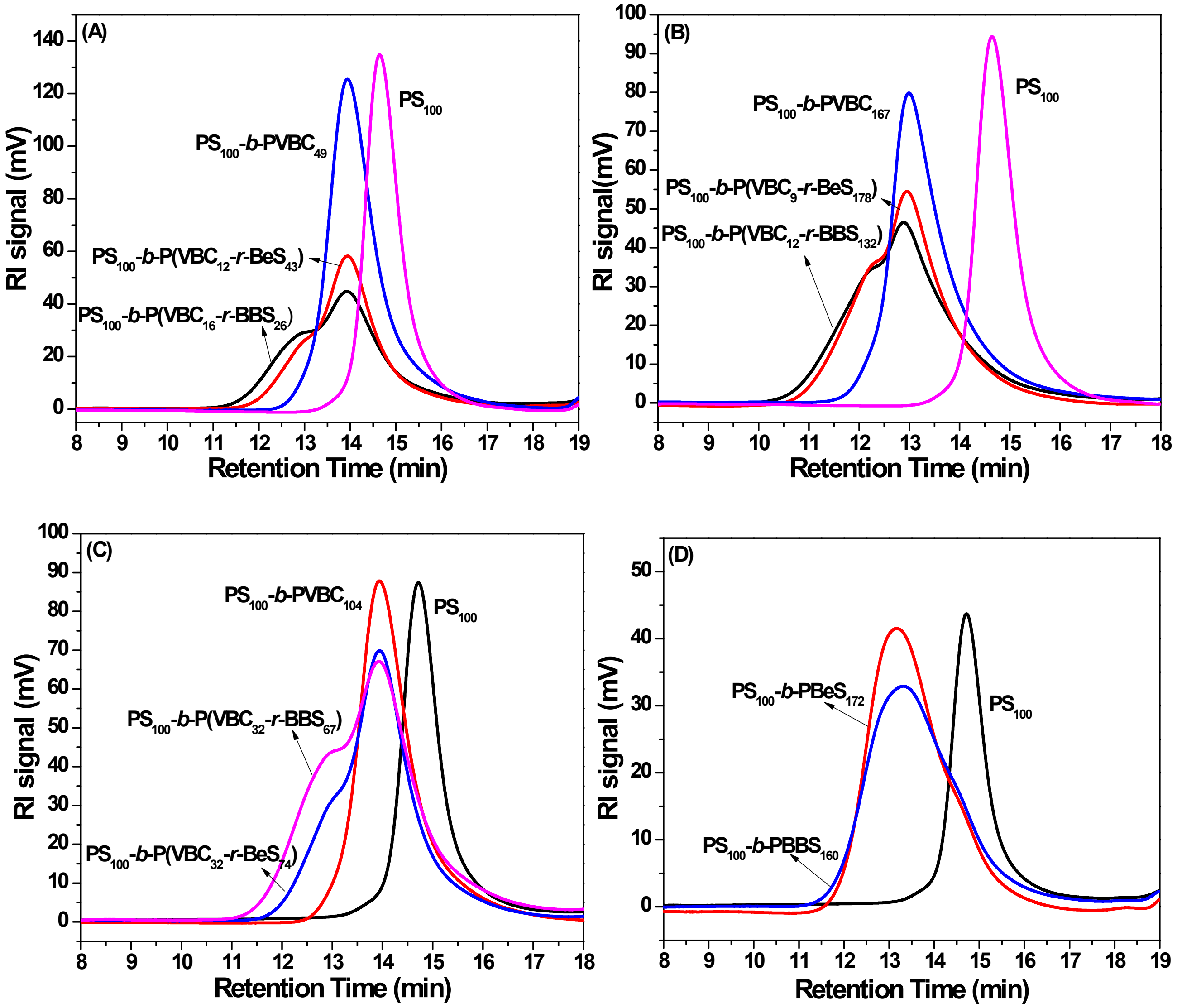


Figure S1. GPC plots of macroinitiator PS$_{100}$, PS-*b*-PVBC, PS-*b*-P(VBC-*r*-BeS), PS-*b*-P(VBC-*r*-BBS), PS-*b*-PBeS and PS-*b*-PBBS block copolymers.

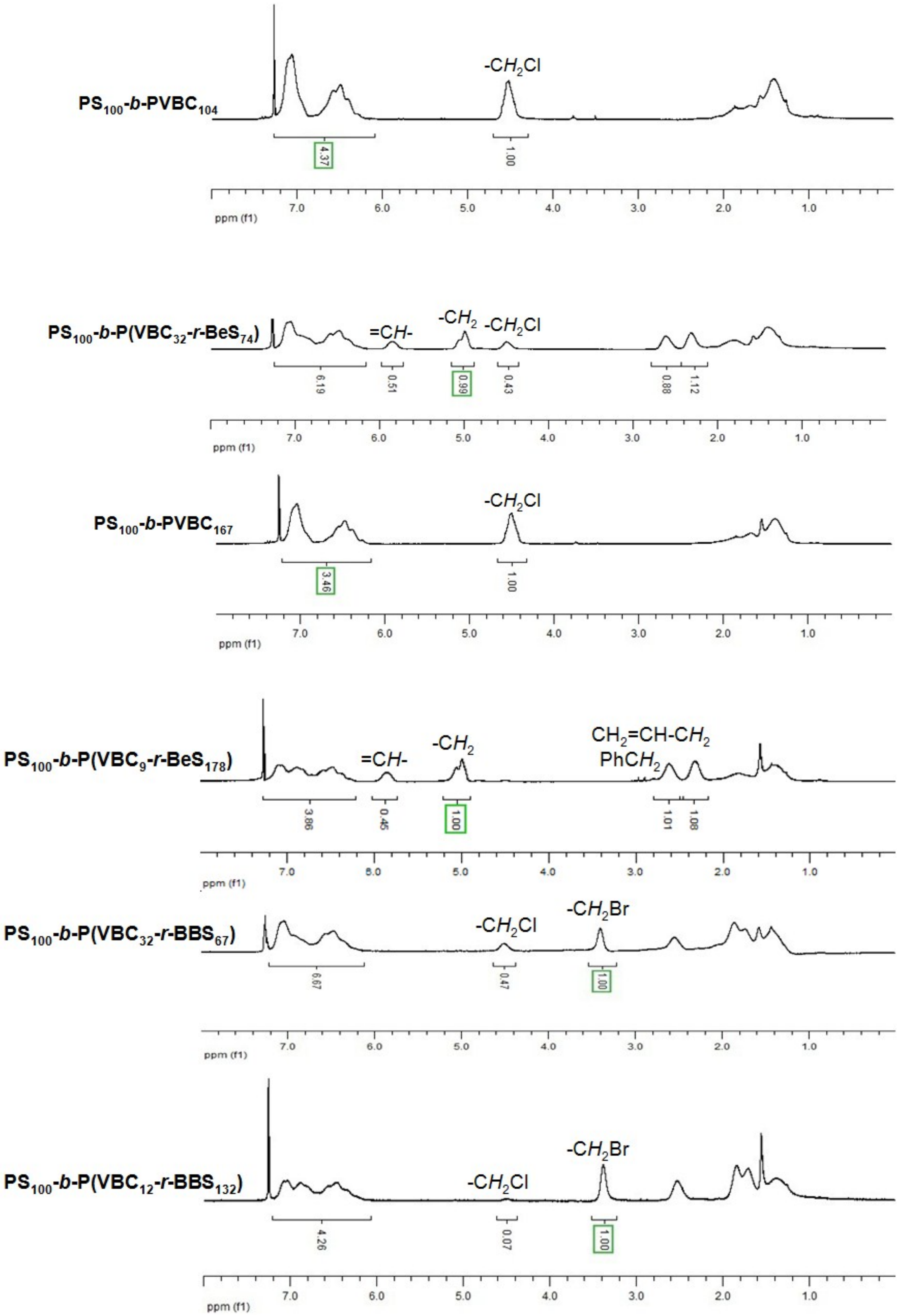


Figure S2. ^{1}H NMR spectra of PS-*b*-PVBC, PS-*b*-P(VBC-*r*-BeS) and PS-*b*-P(VBC-*r*-BeS) block copolymers.

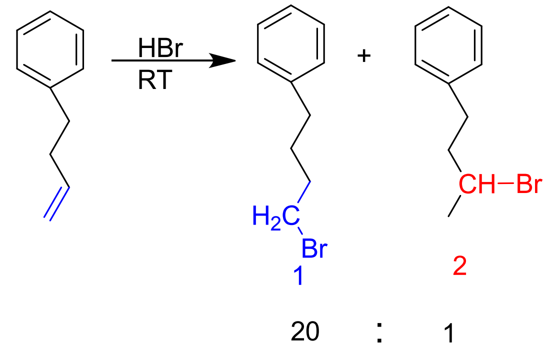
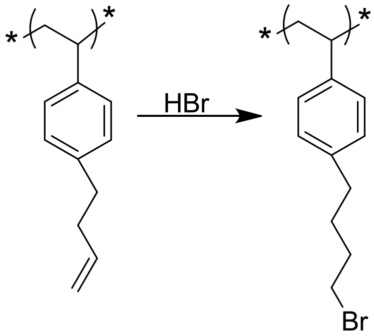


Figure S3. HBr Addition to 4-butenylbenzne.

Generally, HBr addition to double bonds generates the Markovnikov product **2** in which the external Br atom is not in the terminal position. However, under peroxides or UV light conditions, the regioselectivity is anti-Markovnikov to predominantly produce 4-bromobutylbenzene terminal addition product **1** as demonstrated in our work. The ratio of 1, major product, to 2, side reaction, is 20, based on ^{1}H NMR.



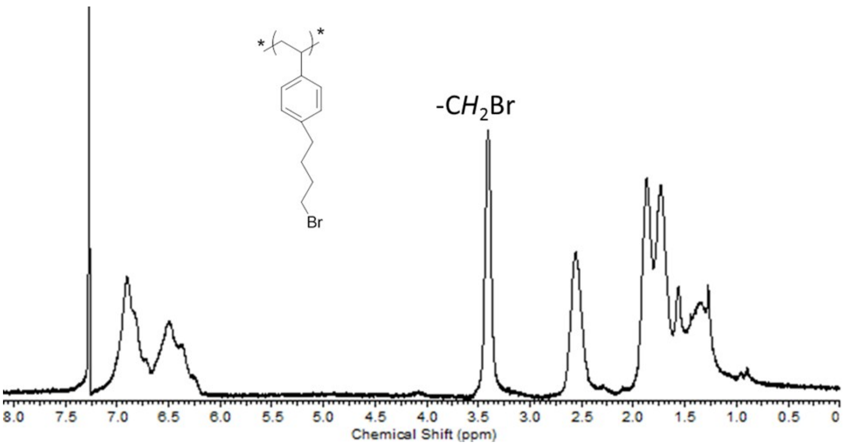


Figure S4. HBr Addition to model homopolymer poly(4-butenylstyrene).

When HBr addition comes to the model homopolymer, there is no observable peak at 4.0 ppm. This indicated 100% transformation of CH_2=CH- double bonds to CH_2BrCH_2-.

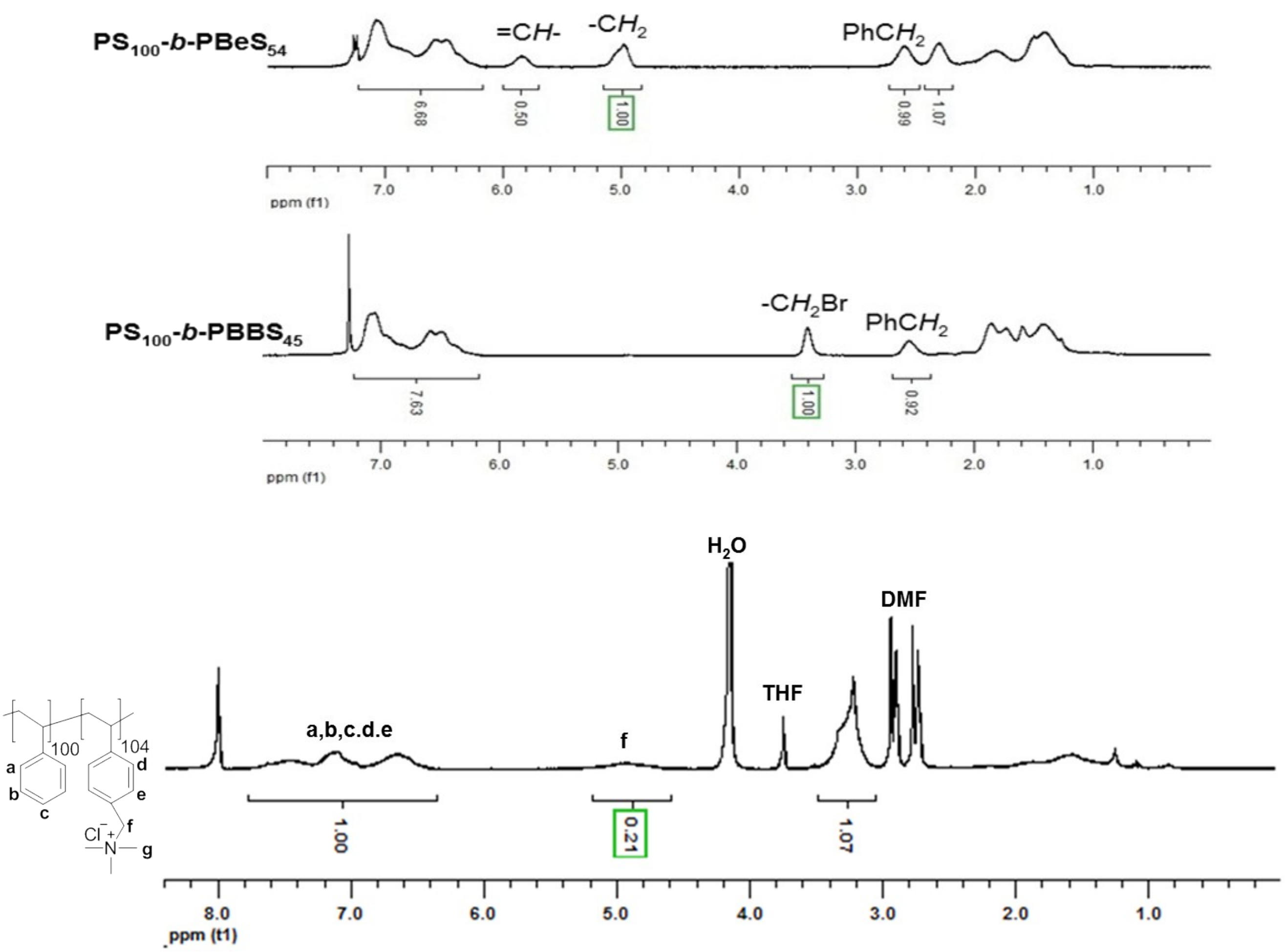


Figure S5. Model reactions of HBr terminal addition to olefinic double bonds, top line and ^{1}H NMR spectra of PS-*b*-PBeS and PS-*b*-PBBS block copolymers in $CDCl_3$ at 25 °C and Q- PS_{100}-*b*-$PVBC_{104}$ in d_7-DMF/CD_3OD (trace).

Table S1. Properties of Synthesized Block Copolymer Anion Exchange Membranes.

Sample	IEC (NMR)	d(SAXS)[a] (nm)	d(SAXS)[b] (nm)	Conductivity[a] (mS cm^{-1})	Conductivity[b] (mS cm^{-1})
Q-PS$_{100}$-*b*-PBBS$_{160}$	3.15	27	19	NA	33.7
Q-PS$_{100}$-*b*-PVBC$_{104}$	3.20	33	NA	20.4	28.9
Q-PS$_{100}$-*b*-P(VBC$_{12}$-*r*-PBBS$_{132}$)	3.18	24	NA	18.7	25.2
Q-PS$_{100}$-*b*-PVBC$_{167}$	3.66	39	28	26.5	36.6

IEC of Q-PS$_{100}$-*b*-PBBS$_{160}$ was calculated by chloride form after ion exchange with 1M aqueous NaCl; conductivity was measured at 30 °C under 95% relative humidity in chloride form; a, the membranes were cast from toluene/1-propanol (v/v = 1:1) except Q-PS$_{100}$-*b*-PBBS$_{160}$ was cast from chloroform/1-propanol/methanol (v/v/v = 2:1:1); b, the samples were prepared from DMF/1-propanol (v/v = 3:1).

Table S2. Different Side Chain Block Copolymers from Corresponding Copolymer Precursors.

Sample	Butene	Grignard Precursor
PS$_{100}$-*b*-PBBS$_{45}$	PS$_{100}$-*b*-PBeS$_{54}$	NA
PS$_{100}$-*b*-PBBS$_{160}$	PS$_{100}$-*b*-PBeS$_{172}$	NA
PS$_{100}$-*b*-P(VBC$_{16}$-*r*-PBBS$_{26}$)	PS$_{100}$-*b*-P(VBC$_{11}$-*r*-PBeS$_{44}$)	PS$_{100}$-*b*-PVBC$_{49}$
PS$_{100}$-*b*-P(VBC$_{32}$-*r*-PBBS$_{67}$)	PS$_{100}$-*b*-P(VBC$_{32}$-*r*-PBeS$_{70}$)	PS$_{100}$-*b*-PVBC$_{104}$
PS$_{100}$-*b*-P(VBC$_{12}$-*r*-PBBS$_{132}$)	PS$_{100}$-*b*-P(VBC$_{33}$-*r*-PBeS$_{134}$)	PS$_{100}$-*b*-PVBC$_{167}$

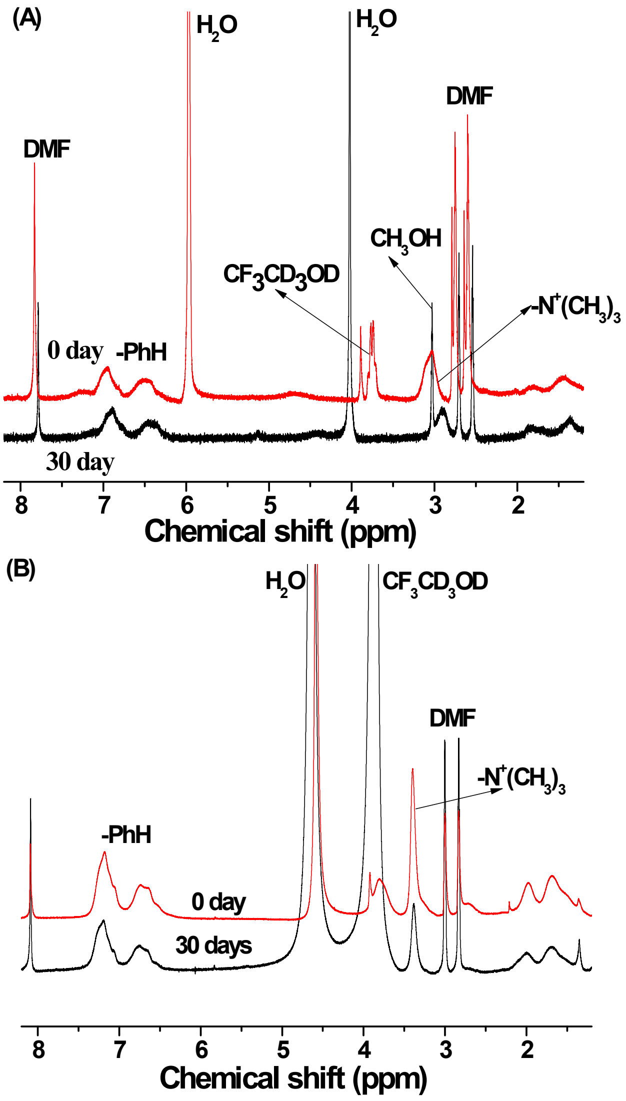


Figure S6. ^{1}H NMR spectra of (A) quaternized C4 side chain Q-PS$_{100}$-*b*-PBBS$_{45}$ and (B) benzyltrimethyl ammonium copolymer powder from Q-PS$_{100}$-*b*-PVBC$_{49}$ in 1M NaOD at 80 °C for 30 days. -PhH denotes aromatic protons.

$$\text{Cations remaining} = (\text{ratio of } H_i/H_{aromatic})_t/(\text{ratio of } H_i/H_{aromatic})_0$$

Where H_i is the integration of methyl protons on ammonium cations, $H_{aromatic}$ is the sum of aromatic protons, $(H_a+H_b+H_c+H_d+H_e)$ on the aromatic rings.

Block Copolymer Morphology and Interdomain Spacing Illustrations.

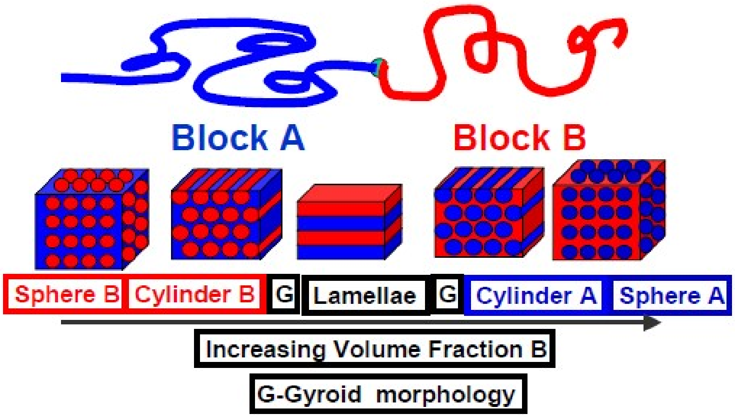


Figure S7. Classical morphology of the block copolymer indicated by TEM images.

AB diblock copolymer would generate the following stable microstructures: lamellae (LAM), hexagonal-packed cylinder (Hex), body centered cubic sphere (BCC), closed-packed sphere (FCC) and bicontinuous gyroid structure (Gyr), depending upon the volume fraction of a component as shown in **Figure S7.**[1]

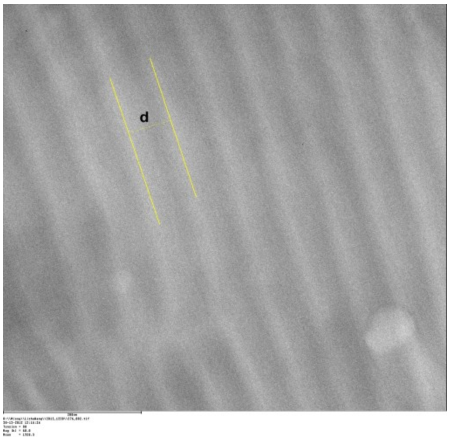


Figure S8. TEM image of PVBC-*b*-PBeS diblock copolymer with lamellar microstructure.[2]

The interdomain spacing of block copolymers is the interplanar distance of the periodic lattice formed by the chemically different blocks. For example, the interdomain spacing of our lab-made quaternized poly(vinylbenzyl chloride)-*b*-poly(butenylstyrene) (Q-PVBC-*b*-PBeS) is the plane to plane spacing of

54 nm as shown in **Figure S8** while the cylindrical periodicity of poly(styrene)-*b*-poly(butadiene) (PS-*b*-PB) copolymer is the center to center distance of 23 nm (more information see reference 2).

Table S3. Peak ratio of SAXS patterns for various structures.[3]

Structure	Ratio q/q*
Lam	1, 2, 3, 4. 5, 6, …
Hex	$1, \sqrt{3}, \sqrt{4}, \sqrt{7}, \sqrt{9}, \sqrt{12}, \ldots$
BCC	$1, \sqrt{2}, \sqrt{3}, \sqrt{4}, \sqrt{5}, \sqrt{6}, \ldots$
FCC	$1, \sqrt{4/3}, \sqrt{8/3}, \sqrt{11/3}, \sqrt{12/3}, \sqrt{16/3}, \ldots$
Gyr	$1, \sqrt{4/3}, \sqrt{7/3}, \sqrt{8/3}, \sqrt{10/3}, \sqrt{11/3}, \ldots$

The interdomain spacing and the morphology of the block copolymers can be predicted and visualized by SAXS and TEM, respectively. From the ratio of peaks in SAXS patterns, the block copolymer morphology is determined as shown in **Table S3**. The interdomain spacing is determined by the equation: $d = 2\pi/q$, where q is the principal peak in SAXS. Furthermore, the interdomain spacing and the morphology are confirmed from TEM images as depicted in **Figure S8**.

References

1. J.M.G. Cowie, Developments in Block Copolymers-I, In I Goodman (Ed.), 1982, Applied Science Publishers, London, P.1-37.

2. T. Lee, N. Yao, H. Imai, I. A. Aksay, *Langmuir* 2001, **17**, 7656.

3. I.W. Hamley, V. Castelletto, *Prog. Polym. Sci.* 2004, **29**, 909.