Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Informations for

Unique Embossed Carbon Layer from Induced Domain Alignment in Block Copolymer Thin Film under Electric Field

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Experimental Details

Materials

Poly(acrylonitrile-*b*-methylmethacrylate) (M_n, PAN=24 kg/mol, PMMA=27 kg/mol, M_w/M_n=1.11) were purchased from Polymer Source and used without further purification.

Spin Coating

PAN-*b*-PMMA thin films were obtained by spin coating at 6000 rpm for 90 s from a 1–2 wt.% DMF solution on a passivated silicon substrate. (International Wafer Source, Inc.)

Application of electric field

A schematic diagram describing the manner in which the electric field was applied is shown in Figure S1. A silicon wafer, coated with thin film, served as one electrode, and a soda-lime glass coated with a thin layer of gold (20 nm) and chromium (5 nm) was the second electrode. A rectangular well was etched in the glass slide by immersion in buffered HF using a poly(methyl methacrylate) mask. The electrode spacing was controlled by varying the etching time: 0.2 μm/min. In this geometry, the dominant gradient in the electric field occurs across the film interface, noted by "d" in Figure S1. A voltage was applied, and the assembly was heated well above the glass transition temperature of polymer. Then the assembly was quenched to room temperature to freeze the EHD pattern. After each experiment, the upper glass electrode was removed mechanically.

Instrumentations

Scanning force microscopy (SFM) images were obtained in both the height and phase-contrastmode using a Digital Instruments Dimension 3100 scanning forcemicroscope in tapping mode. Infrared spectra were obtained by a Bomem MB100 Fourier Transform Infrared (FT-IR) spectrometer with a resolution of 4 cm^{-1}. The Raman spectrum was obtained on a Jobin-Yvon T64000 spectrometer with a laser of a wavelength of 632 nm. SAXS pattern was obtained with a Bruker AXS Nanostar small angle X-ray scattering spectrometer with a generator voltage of 40 KVand a current of 35 mA.

Experimental Apparatus

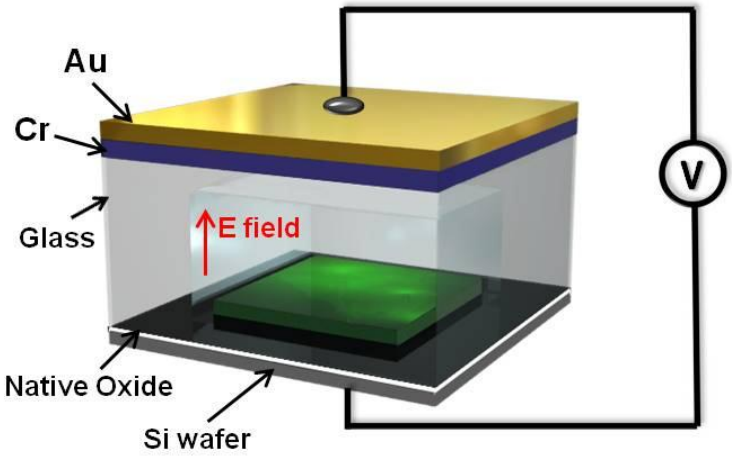

Figure S1. Experimental apparatus for application of electric field to block copolymer thin film.

Carbonization Profile

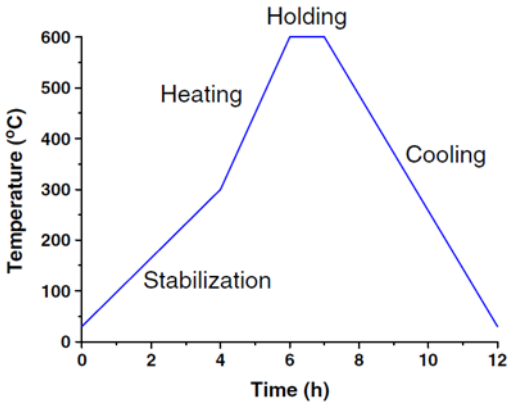

Figure S2. Temperature profile for the carbonization of PAN-*b*-PMMA thin film exposed to electric field. It is composed of stabilization (1 °C/min to 300 °C), heating (3 °C/min to 600 °C), holding, and natural cooling.

SAXS Pattern

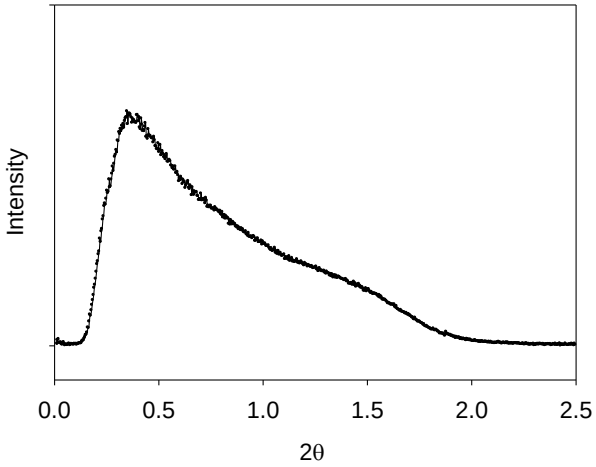

Figure S3. (a) Small angle X-ray scattering pattern of PAN-*b*-PMMA (24 K-27 K) bulk film thermally annealed at 180 °C for 3 days.

AFM image

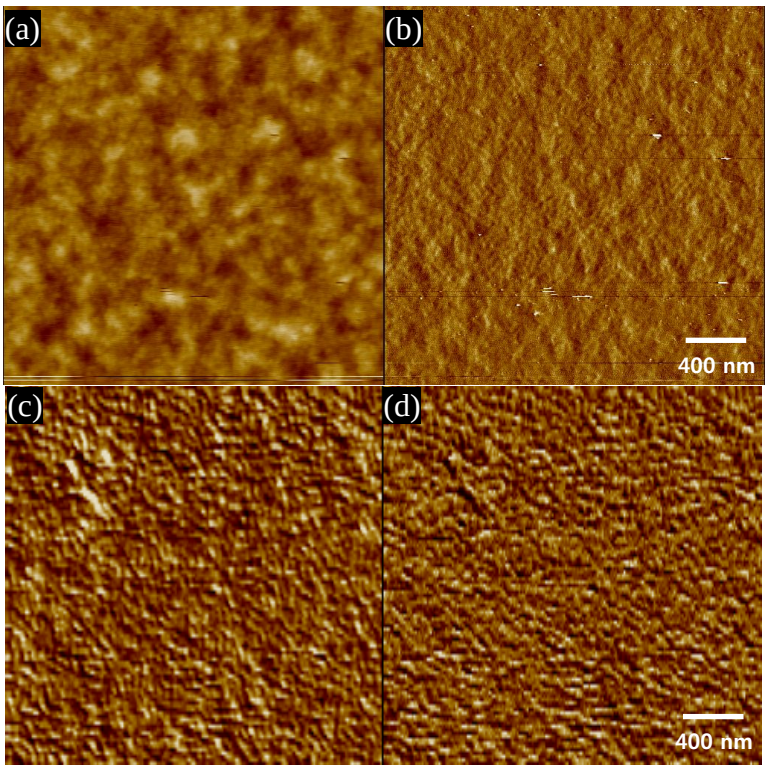

Figure S4. Atomic force microscopy (a) height and (b) phase image of 46 nm PAN-*b*-PMMA (24 K-27 K) thin film exposed to 5 V/μm electric field for 16 h at 180 °C. Atomic force microscopy (c) height and (d) phase image of carbonized PAN-*b*-PMMA (24 K-27 K) thin film in (a) and (b).

AFM PAN-*b*-PMMA 90 nm film

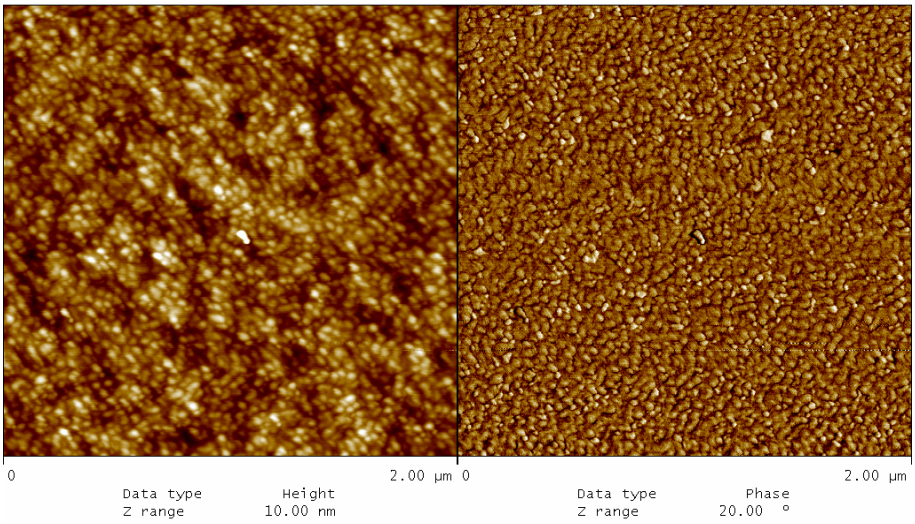

Figure S5. Atomic force microscopy height and phase image of 90 nm PAN-*b*-PMMA (24 K-27 K) thin film after exposure to electric field 10 V/µm for 12 h at 180 °C.

AFM PAN-*b*-PS 50 nm film

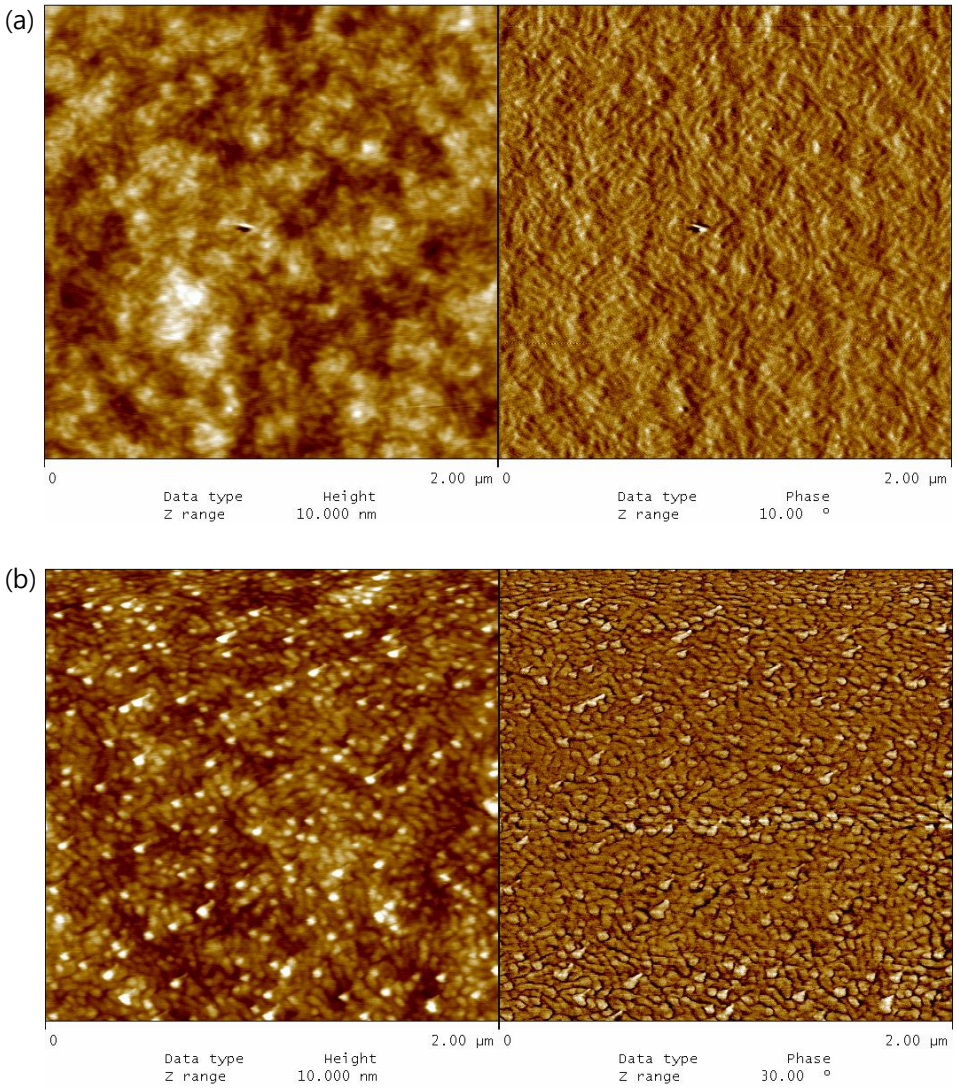

Figure S6. AFM images of PAN-*b*-PS (13 K-15 K) thin film (50 nm) (a) thermally annealed (180 °C for 2 days) and (b) exposed to electric field 10 V/µm for 12 h at 180 °C.

Nanoindentation experiment

Figure S7 shows the displacement-force curve for pristine PAN-*b*-PMMA thin film and the film after exposure to electric field. The force is presented against the difference between the displacement of the sample in the vertical axis, z, and the cantilever deflection, d. The variable z - d is the relative displacement between the tip and the polymer surface. At low values of z - d there is no contact between the tip and the surface (both the deflection of the cantilever and the measure force are near zero). The black line is obtained during indentation while the red one corresponds to the retracting scan. The difference between the indentation and retraction curves is a consequence of the attraction between the tip and the material, the higher the adhesion the bigger the difference. (*Ref : Eur. Polym. J. 2006, 42, 1378*)
Compared with pristine thin film, it is difficult to see the difference. From this fact, it is seen that electric field application did not influence the physical nature of thin film.

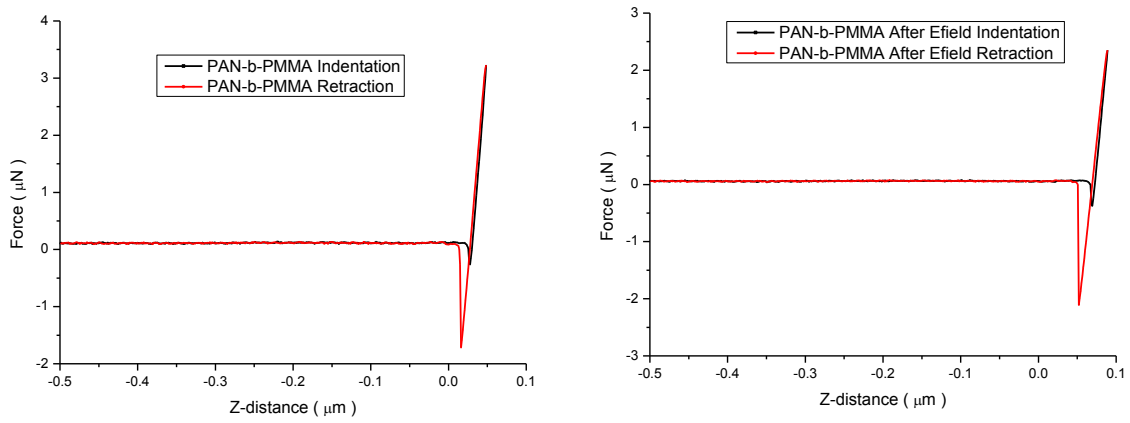

Figure S7. A typical curves for PAN-*b*-PMMA thin film (a) pristine and (b) exposed to electric field showing measured force in an indentation AFM experiment against the difference between the z displacement of the sample and the cantilever deflection d. The black line represents the indentation scan and the thin one the retraction one.

Nanoindentation along parallel lines

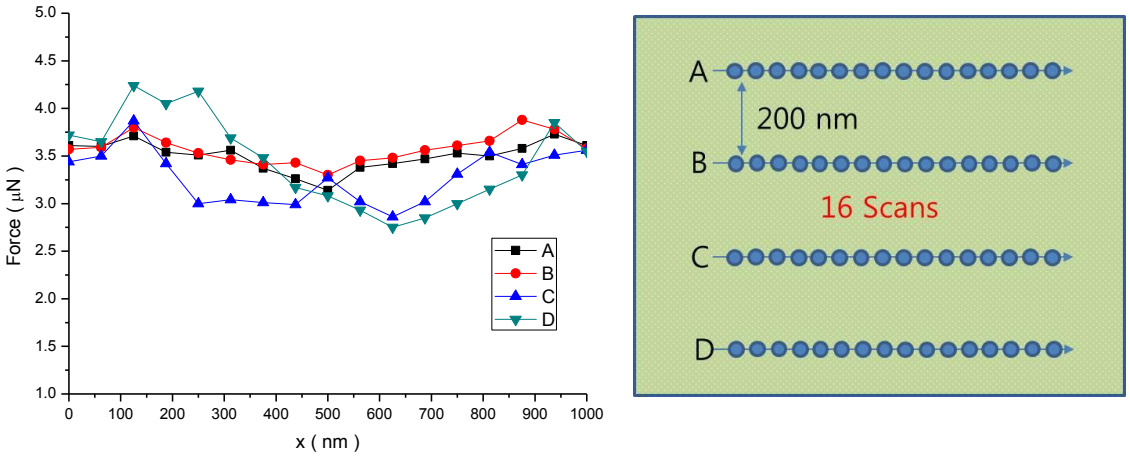

Figure S8. Force plots measured by AFM indentation experiments in PAN-*b*-PMMA thin film exposed to electric field along four parallel lines separated by 200 nm from each other.

Solvent Annealing

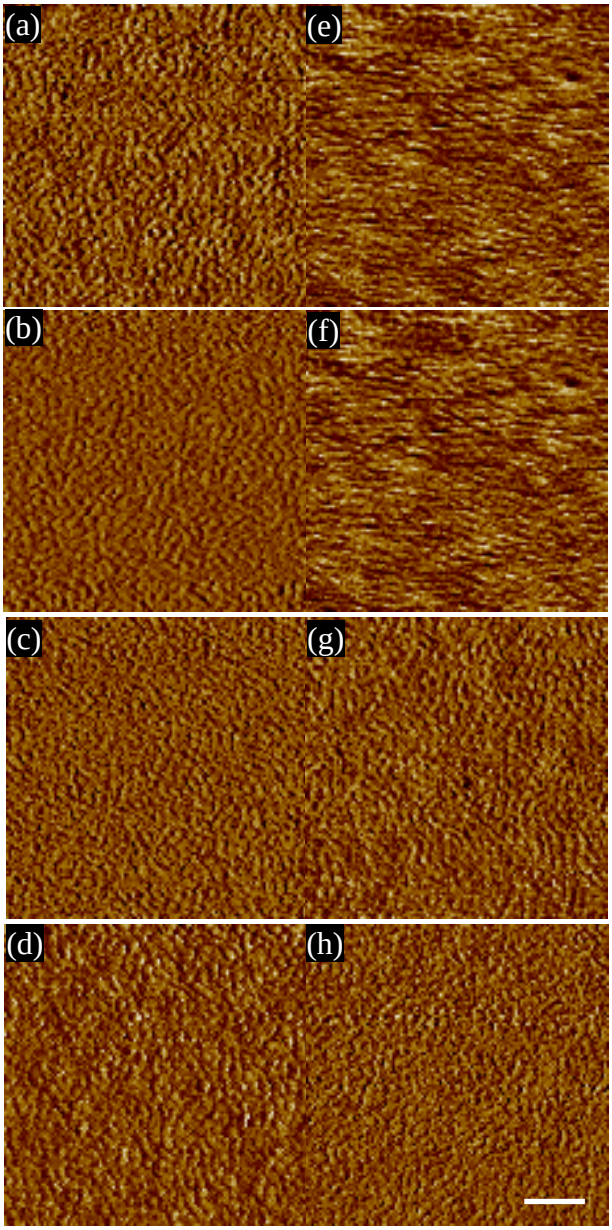

Figure S9. Atomic force microscopy images of solvent annealed PAN-*b*-PMMA block copolymer thin films under toluene for (a) 1 h, (b) 6 h, (c) 12 h, (d) 24 h, and tetrahydrofuran for (e) 1 h, (f) 6 h, (g) 12 h, and (h) 24 h. Scale bar 400 nm.

XPS for carbon film

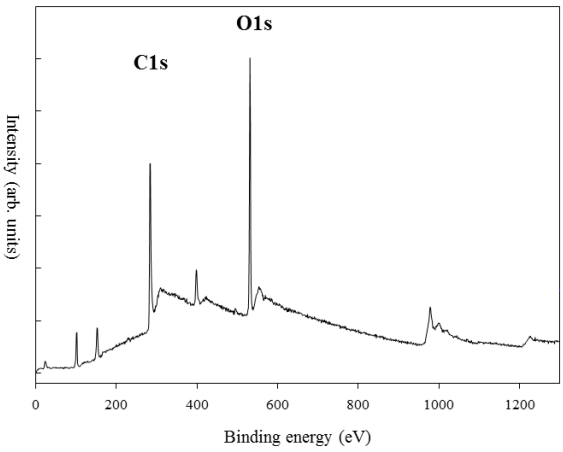

Figure S10. XPS profile of carbon film from PAN-*b*-PMMA copolymer precursor after exposure to electric field.

Nanoindentation for carbon

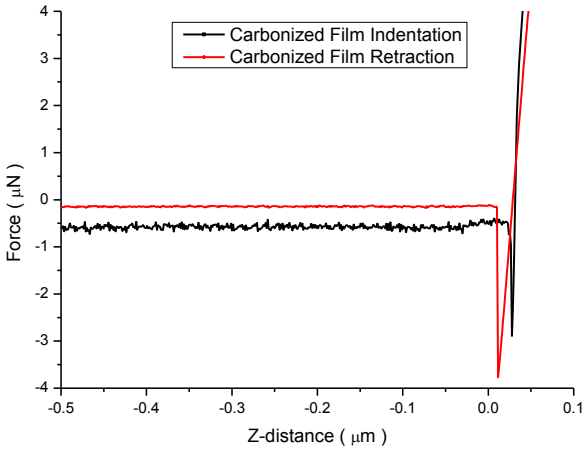

Figure S11. A typical nanoindentation curve for carbonized film after exposure to electric field.

Nanoindentation for carbon along parallel lines

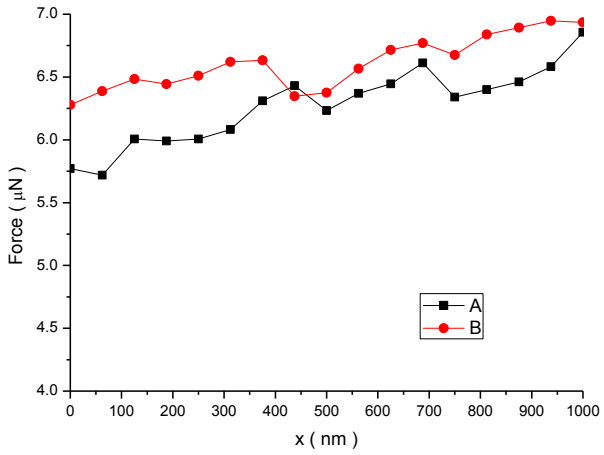

Figure S12. Force plots measured by AFM indentation experiments in carbonized thin film exposed to electric field along two parallel lines separated by 200 nm from each other.