

Spatial Arrangement of Block Copolymer Nanopatterns Using Photoactive Homopolymer Interfaces

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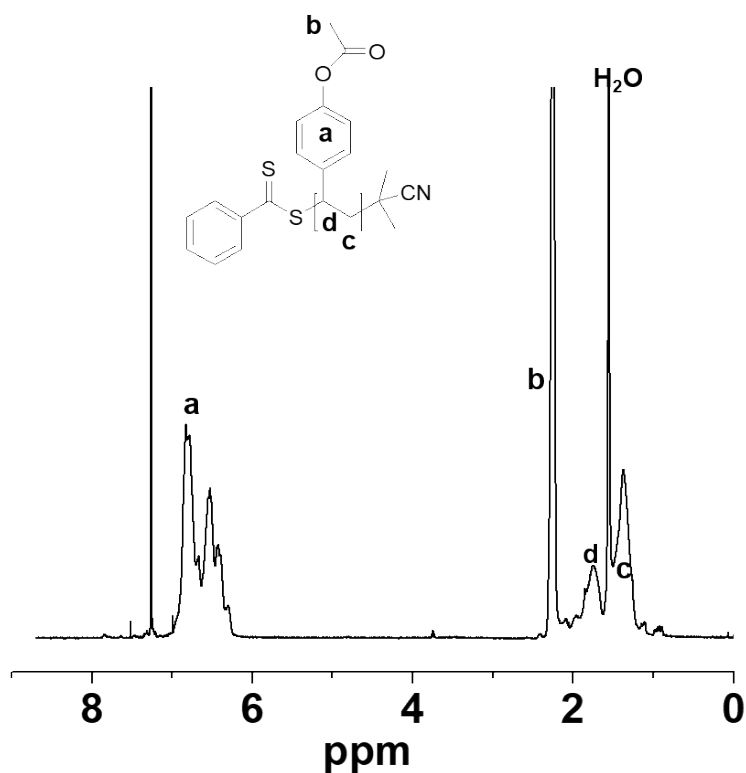


Figure S1. ¹H NMR spectrum of poly(4-acetoxystyrene) in deuteriochloroform.

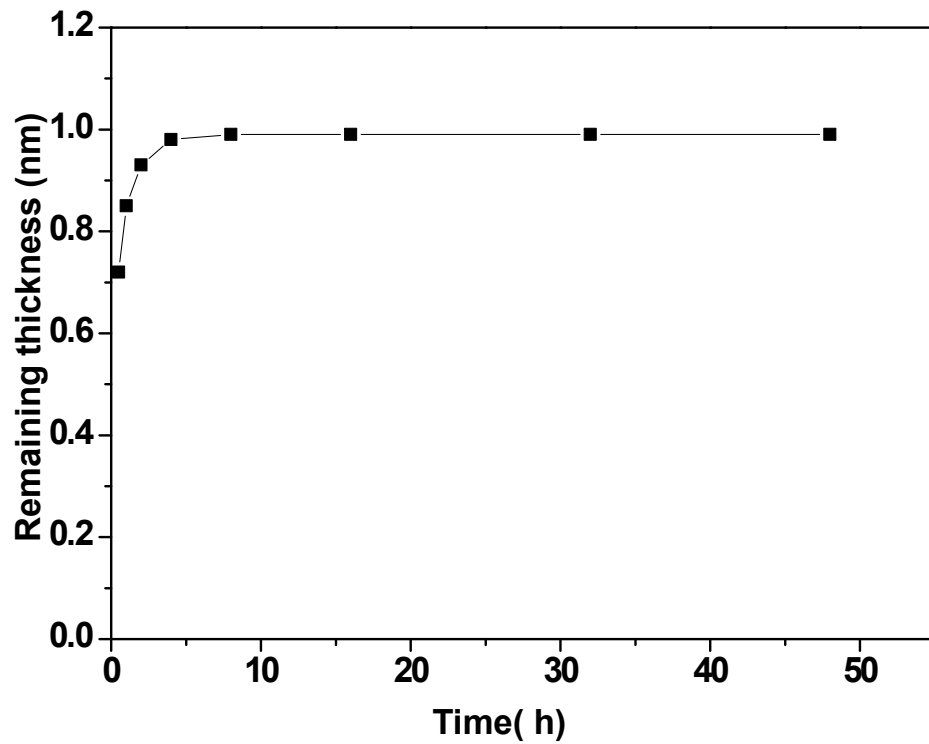


Figure S2. The extent of poly (4-acetoxystyrene) cross-linking as quantified by the normalized residual film thickness as a function of the thermal annealing time.

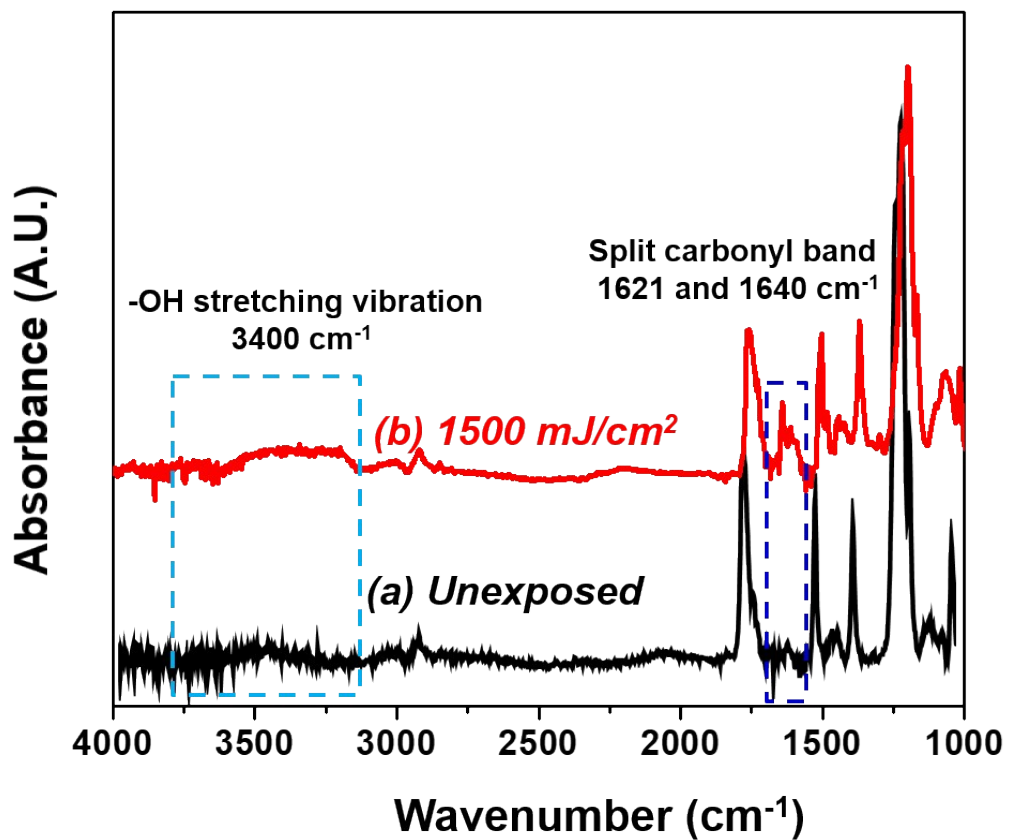


Figure S3. GATR FTIR spectra of thin films of poly(4-acetoxystyrene) thin film after exposure to UV nm light at dose of 1500 mJ/cm^2 .

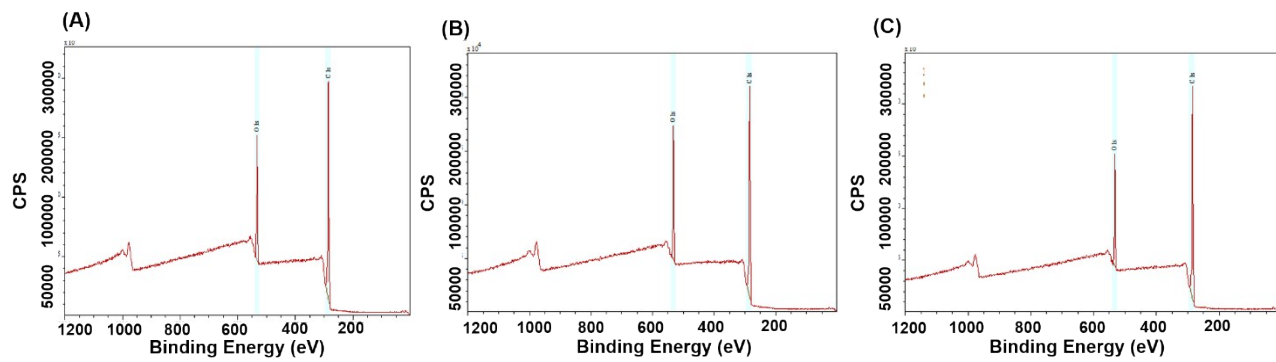


Figure S4. XPS survey scan spectra of poly(4-acetoxystyrene thin films before (A) and after illumination with UV-light (B), followed by posttreatment with benzoyl chloride (C).

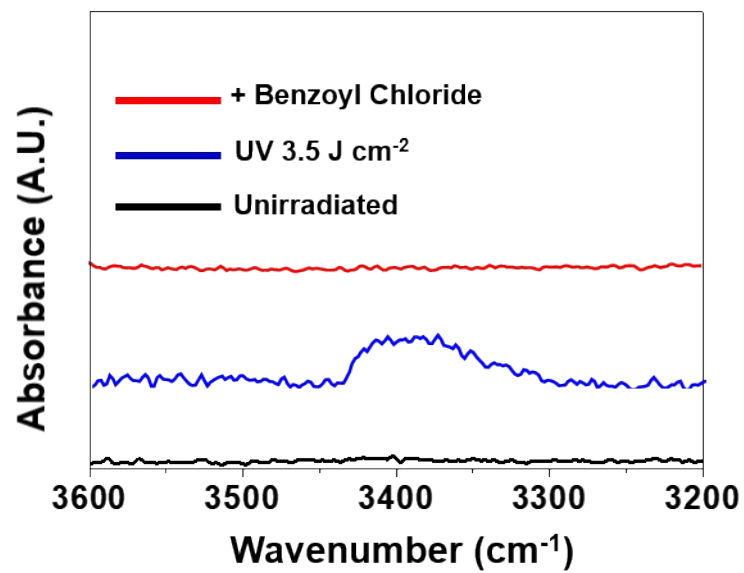


Figure S5. GATR spectra from 3200-3600 cm⁻¹ of poly(4-acetoxystyrene) before and after illumination with UV-light, followed by post treatment with benzoyl chloride.

Table S1. Contact Angle (θ) for poly(4-acetoxystyrene) after post-exposure modification with mixtures of acetyl chloride and 1-naphthoyl chloride at different ratios.

F1-naphthoyl chloride	0 mol%	20 mol%	32 mol%	48 mol%	64 mol%	78 mol%	100 mol%
θ_{H_2O}	75.1 ± 0.8 °	77.4 ± 0.6 °	79.2 ± 0.3 °	81.8 ± 0.2 °	84.3 ± 0.5 °	86.3 ± 0.5 °	88.5 ± 0.7 °
$\theta_{CH_2I_2}$	31.2 ± 0.2 °	33.8 ± 0.9 °	35.3 ± 0.5 °	37.8 ± 0.3 °	38.4 ± 0.7 °	39.6 ± 0.2 °	41.4 ± 0.8 °

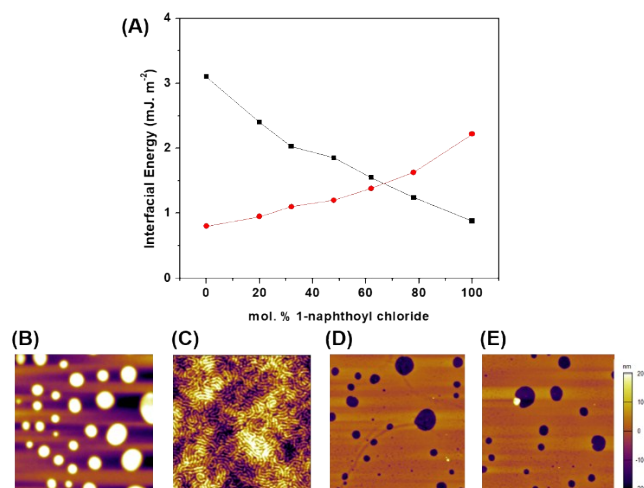


Figure S6. (A) Interfacial energies of PS (black) and PMMA (red) blocks against the post-exposure modified poly(4-acetoxystyrene) substrate plotted against 1-naphthoyl chloride content. AFM height images of PS-*b*-PMMA films annealed at 190 °C for 24h in vacuum placed on modified substrates at different 1-naphthoyl chloride content 0 mol% (B), 64% mol (C), 78% mol (D), 100% mol (E). The film thickness of PS-*b*-PMMA thin film was 1.7 L0.

An alternative method for achieving control of surface energy of the substrate is to functionalize the irradiated poly(4-acetoxystyrene) with specific mixtures of acid chlorides of dissimilar intrinsic surface activity. As a proof-of-principle, mixtures of acetyl chloride and 1-naphthoyl chloride were used to functionalise poly(4-acetoxystyrene) films exposed to UV light (3.5 J cm⁻²) at which dose the maximum yield of hydroxyketone groups was achieved. Table S1 lists the contact angles of poly(4-acetoxystyrene) films modified in this manner. The water contact angles of the modified substrate were found to increase with increasing content of 1-naphthoyl chloride (Table S1), as the naphthyl ester is more hydrophobic than the methyl ester.¹ As shown in Figure S5A, the estimated interfacial energies of PS and PMMA are almost equal when the content of 1-naphthoyl chloride in the mixtures varies from 58-78 mol %. It was shown that the films post-modified with pure acetyl chloride were preferentially wet by PMMA block, i.e. similar to the unexposed films (Figure S5B). A reasonable explanation for the wetting behaviour of the PS-*b*-PMMA thin films is the regeneration of acetoxy groups after post-modification. Perpendicular orientation of the annealed PS-*b*-PMMA was observed when the content of 1-naphthoyl chloride in the reaction mixture was 64 mol % (Figure S5C). In contrast, a “hole” morphology were observed at higher 1-naphthoyl chloride contents as a result of stronger hydrophobicity and higher carbon content of the naphthoyl-substituted groups.² These results demonstrate that poly(4-acetoxystyrene) can be used as a substrate for tuning BCP nanodomain orientation, either by controlling the UV exposure dose, or the composition of the mixture of acid chlorides used in the subsequent functionalization step.

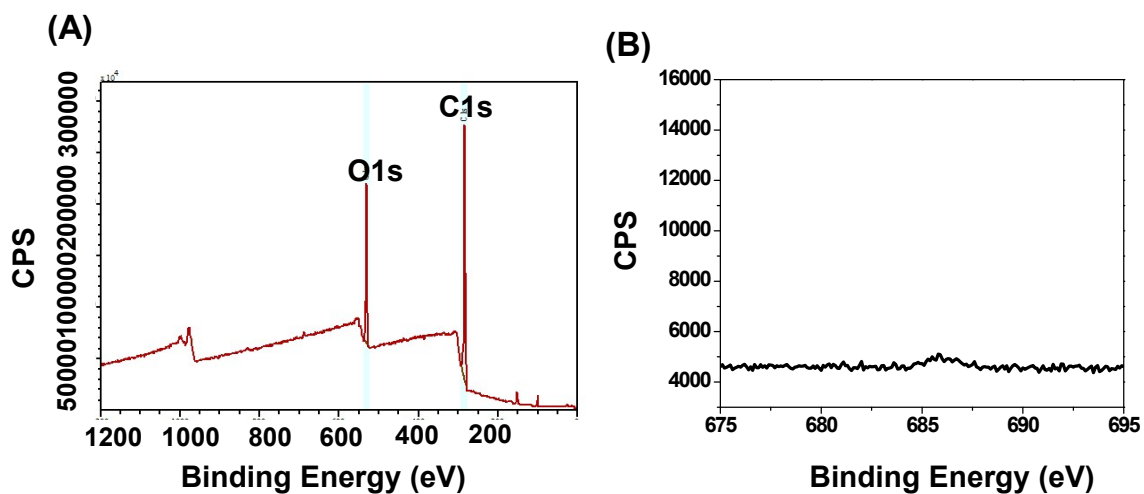


Figure S7. XPS survey scan (A) and high resolution XPS F1s (B) of original poly(4-acetoxystyrene) thin film without e-beam irradiation after treatment with pentafluorophenylhydrazine.

Reference

1. R. R. Thomas and L. E. Stephans, *J. Colloid. Interface Sci.*, 2002, **251**, 339.
2. Y. Pang, L. Wan, G. Huang, X. Zhang, X. Jin, P. Xu, Y. Liu, M. Han, G.-P. Wu and S. Ji, *Macromolecules*, 2017, **50**, 6733.