

## Supporting information

### Synthesis of 6-bromo-3-methylhexa-1,3-diene

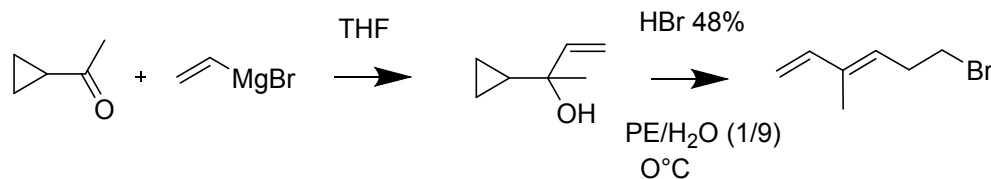


Figure S1: Synthesis of 6-bromo-3-methylhexa-1,3-diene

2-cyclopropylbut-3-en-2-ol was synthesized through a Grignard reaction. 4.23 g of cyclopropyl methyl ketone were added to 50 mL of dry THF and cooled to  $-10^{\circ}\text{C}$ . Under vigorous stirring a solution of vinyl magnesium bromide in THF (55 mmol, 55 mL, 1M in THF) was added over 5 minutes. The reaction mixture was allowed to warm to room temperature and stirring continued for one hour. The reaction was quenched with 10 mL aqueous  $\text{NH}_4\text{Cl}$  and the product was extracted with  $\text{Et}_2\text{O}$  and then washed with water and brine. Organic phases were dried on  $\text{MgSO}_4$  and concentrated to give the crude acrylic alcohol.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): (ppm) 5.75 (dd, 1H,  $\text{CH}=\text{CH}_2$ ), 5.15 (d, 1H,  $\text{CH}=\text{CHH}_{\text{trans}}$ ), 4.94 (d, 1H,  $\text{CH}=\text{CHH}_{\text{cis}}$ ), 1.28 (s, 3H,  $\text{CH}_3$ ), 1.15 (m, 1H,  $-\text{CH}(\text{CH}_2)_2$ ), 0.96 (m, 2H, cyclopropane  $-\text{CH}_2-$ ).

The crude acrylic alcohol was dissolved in petroleum ether and water (5 mL/15 mL) and an aqueous HBr solution was added (48%, 30 mL) at  $0^{\circ}\text{C}$  over a period of 5 minutes. After one hour of stirring, the organic phase was extracted with petroleum ether and then washed with water, saturated aqueous  $\text{NaHCO}_3$  and brine. The organic phases were dried on  $\text{MgSO}_4$ . A flash chromatography was conducted for purification (eluent: petroleum ether,  $r_f = 0.7$ ).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): (ppm) 6.40 (dd, 1H,  $\text{CH}=\text{CH}_2$ ), 5.49 (t, 1H,  $\text{CH}=\text{CH}_2$ ), 5.16 (s, 1H,  $\text{CH}=\text{CHH}_{\text{trans}}$ ), 5.04 (s, 1H,  $\text{CH}=\text{CHH}_{\text{cis}}$ ), 3.39 (m, 2H,  $\text{CH}_2\text{CH}_2\text{Br}$ ), 2.76 (m, 2H,  $\text{CH}_2\text{CH}_2\text{Br}$ ), 1.79 (s, 3H,  $\text{CH}_3$ ).

## Synthesis of PMA-TAD

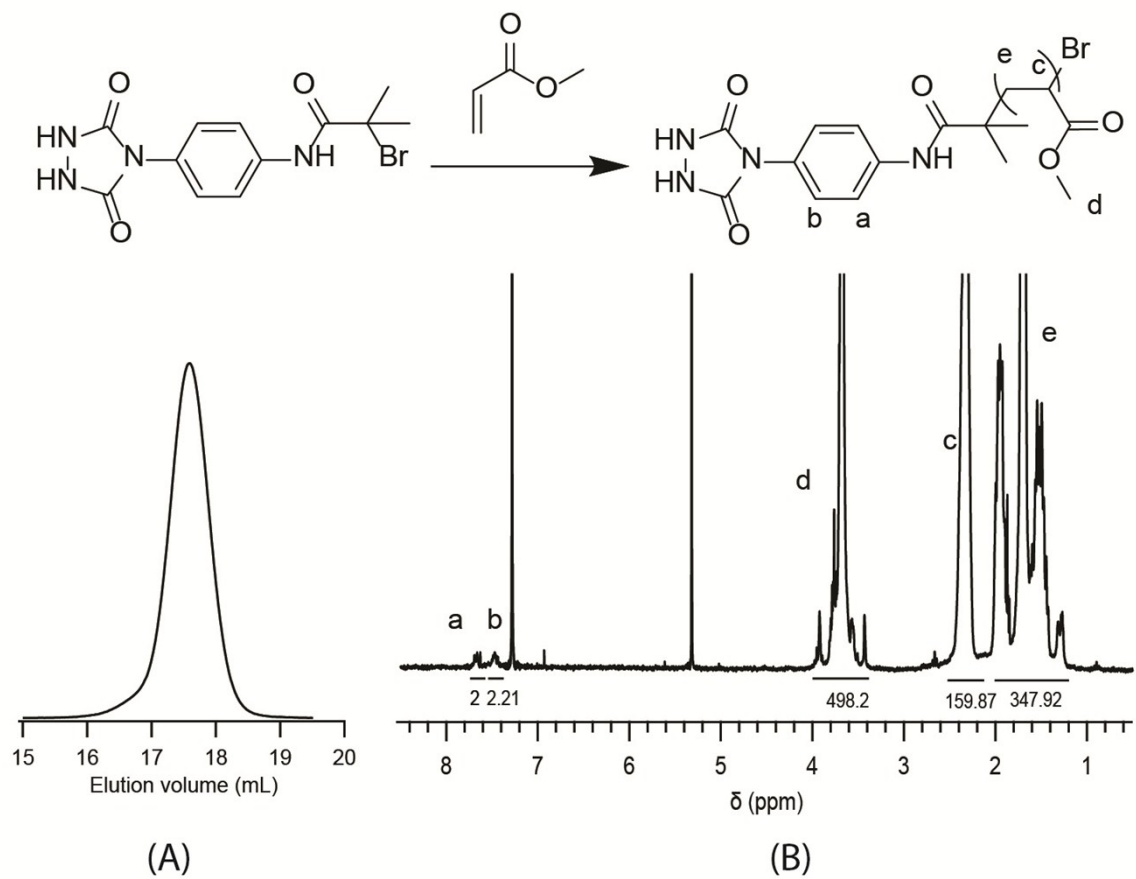


Figure S2: Synthesis of PMA-TAD by SET-LRP. (A) SEC curve and (B) <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> of PMA-TAD

## AFM pictures of diene-functionalised and cross-linked PS-*b*-P4VP

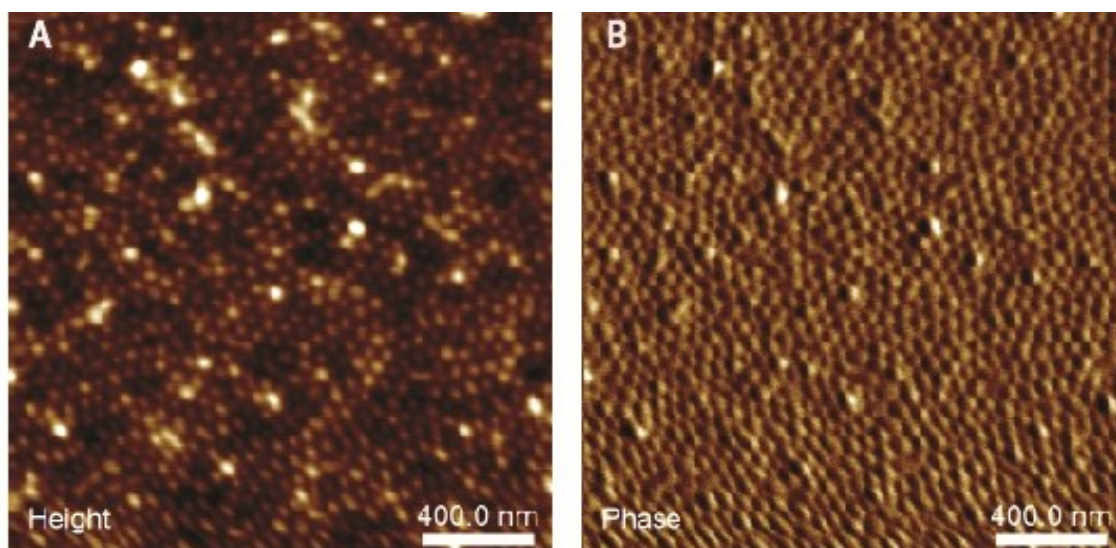


Figure S3: AFM pictures (height and phase) of PS-*b*-P4VP thin films after functionalisation by 6-bromo-3-methylhexa-1,3-diene and cross-linking with 1,4-diiodobutane.