Electronic Supplementary Information for

An ABA triblock containing a central soft block of poly[2,5-di(*n*-hexogycarbonyl)styrene] and outer hard block of poly(4-vinylpyridine): synthesis, phase behavior and mechanical enhancement

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Synthesis of monomer 2,5-di(*n*-hexogycarbonylstyrene) (HCS)

Scheme S1 Synthetic route of HCS

A 500 mL round bottom flask was charged with a solution of *n*-hexanol (6.6 g, 63 mmol) in 250 mL of CH_2Cl_2. To the solution under stirring, vinyl terephthalic acid (5.8 g, 30 mmol), dimethylaminopyridine (DMAP, 0.75 g, 6 mmol) was added followed by DCC (12.6 g, 60 mmol) at room temperature. The solution immediately turned cloudy with white precipitates. After stirring at room temperature overnight, the mixture was filtered and the solution was evaporated. A purified product was easily obtained by passing through a silica gel column. Yield: 60%. ^{1}H NMR ($CDCl_3$, 400

MHz): δ = 7.9-8.30 (s, 3H, in phenyl ring), δ = 7.35-7.50 (q, H, -C*H*=), δ = 5.70-5.80 (d, H, -C*H*=), δ = 5.35-5.50 (d, H, -C*H*=), δ=4.25-4.40 (m, 4H, -OCH_2), δ=1.30-1.90 (m, 16H, -CH_2-), δ=0.80-1.00 (m, 6H, -CH_3). Anal.Calcd. $C_{22}H_{32}O_4$ C: 73.35 H: 9.05 M/Z=360

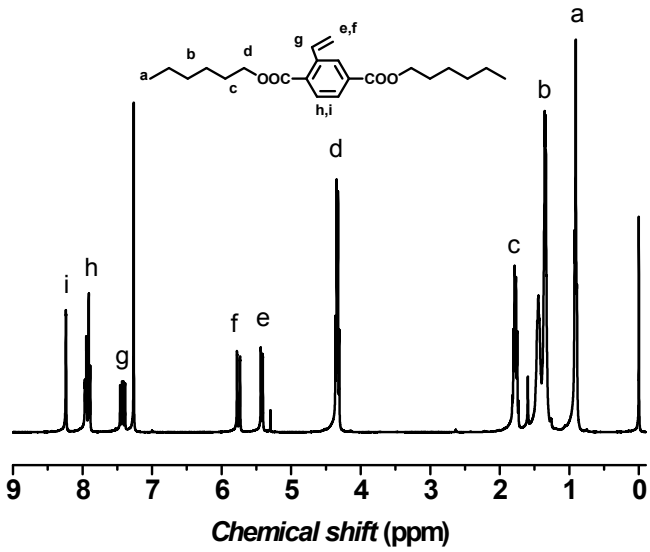

Fig. SI-1 ^{1}H NMR spectrum of 2,5-di(*n*-hexogycarbonyl)styrene (HCS) monomer (Sample in $CDCl_3$, 400 MHz).

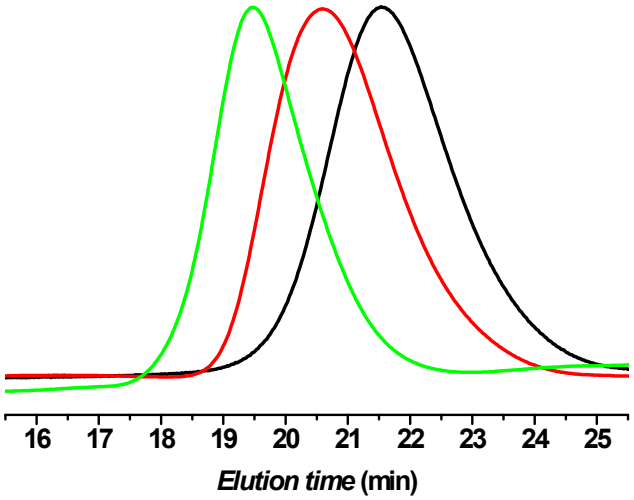

Fig. SI-2 GPC traces of difunctional macroinitiator Cl-PHCS-Cl. From right to left, the traces correspond to the samples with the $M_{n,\,GPC}$ of 11600, 18000, and 33200 g mol^{-1} calibrated with polystyrene standards.

Table SI-1 Molecular weight and polydispersity of difunctional macroinitiator Cl-PHCS-Cl

Sample code [a]	Conversion	$M_{n,\,GPC}$ (g mol^{-1})	$M_{w,\,GPC}$ (g mol^{-1})	PDI	$M_{n,\,LS\text{-}GPC}$ (g/mol)
$PHCS_{51}$	38%	11600	14800	1.28	18400
$PHCS_{77}$	40%	18000	23200	1.29	27600
$PHCS_{123}$	45%	31800	39400	1.24	44500
$PHCS_{130}$	45%	33200	41500	1.25	46900
$PHCS_{157}$	35%	35400	43900	1.24	56600

[a] Sample code $PHCS_X$, where subscript X is the degree of polymerization calculated based on the M_n measured by LS-GPC.

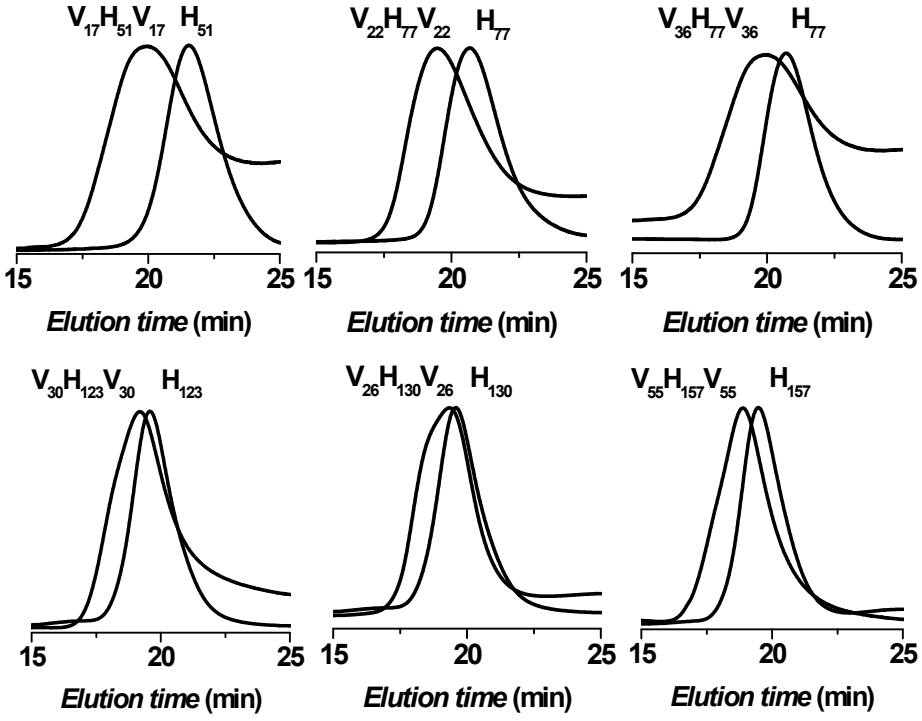

Fig. SI-3 GPC traces of triblocks of P4VP-*b*-PHCS-*b*-P4VP ($V_XH_YV_X$) and the corresponding macroinitiator Cl-PHCS-Cl. THF was used as the eluent at a flow rate of 1.0 ml min^{-1}.

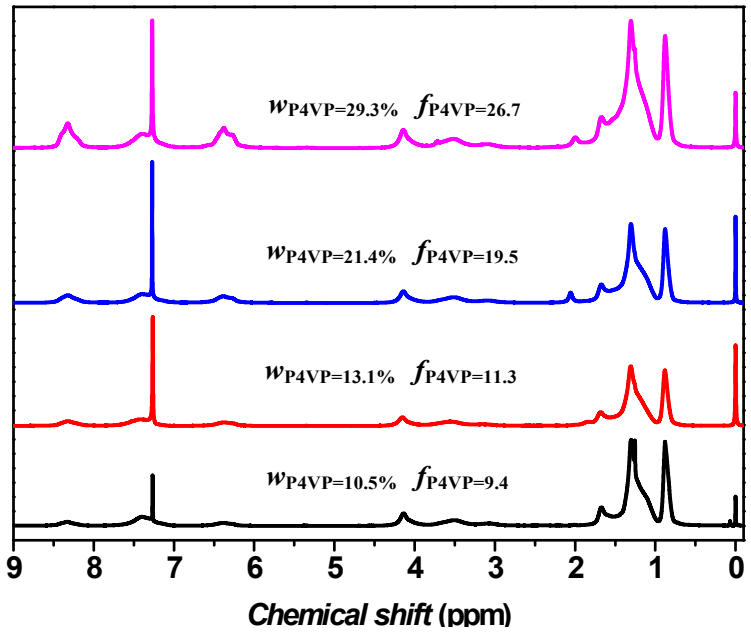

Fig. SI-4 ^{1}H NMR spectra of the P4VP-*b*-PHCS-*b*-P4VP triblock copolymers with various P4VP contents. (samples in $CDCl_3$, 400 MHz).

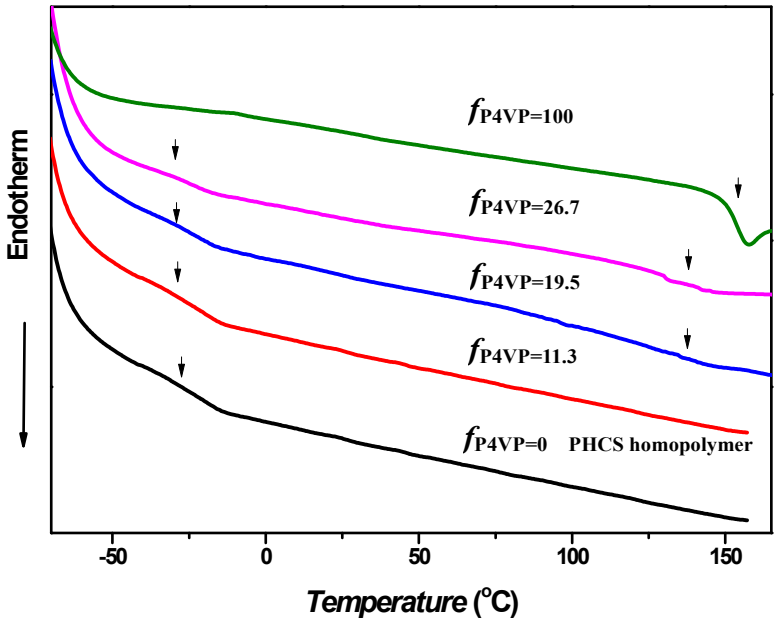

Fig. SI-5 DSC curves of the triblock copolymers with variable f_{P4VP} recorded during the second heating scan at a rate of 40 °C min^{-1}.

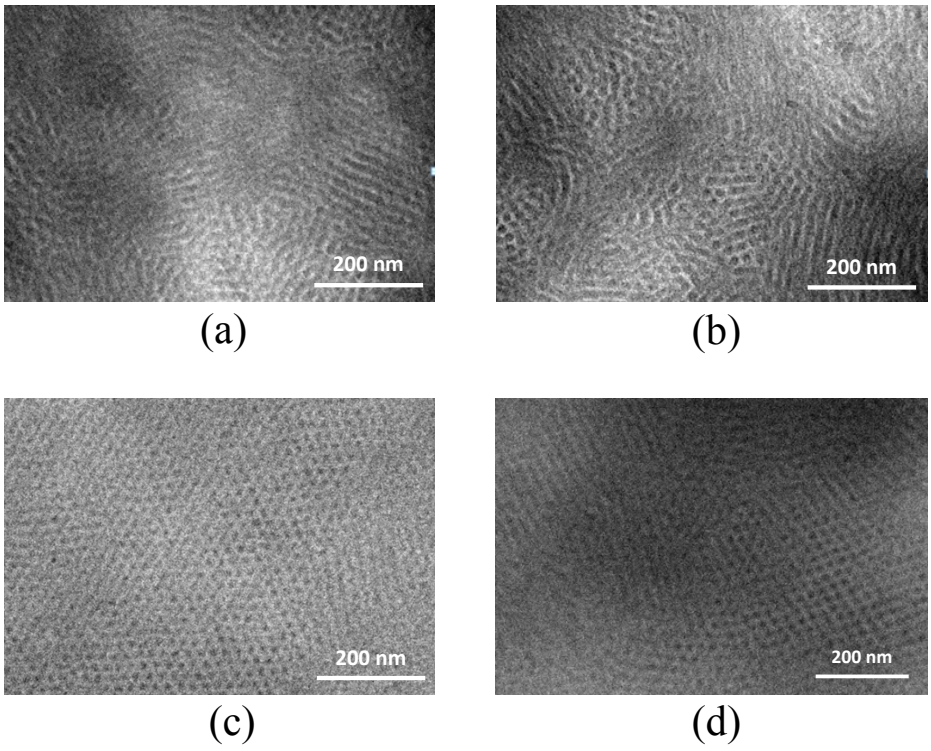

Fig. SI-6 TEM image of $V_{36}H_{77}V_{36}$ (a, b) and $V_{30}H_{123}V_{30}$ (c, d).

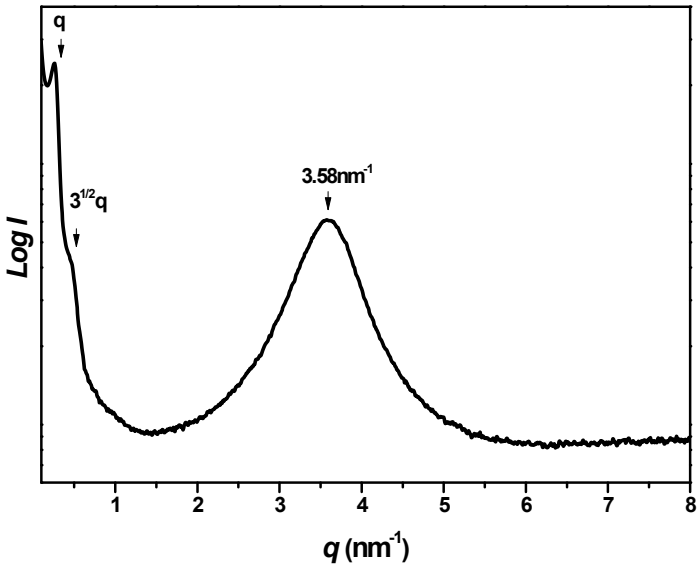

Fig. SI-7 XRD profile of a typical triblock copolymer of $V_{30}H_{123}V_{30}$ recorded at 160 °C.

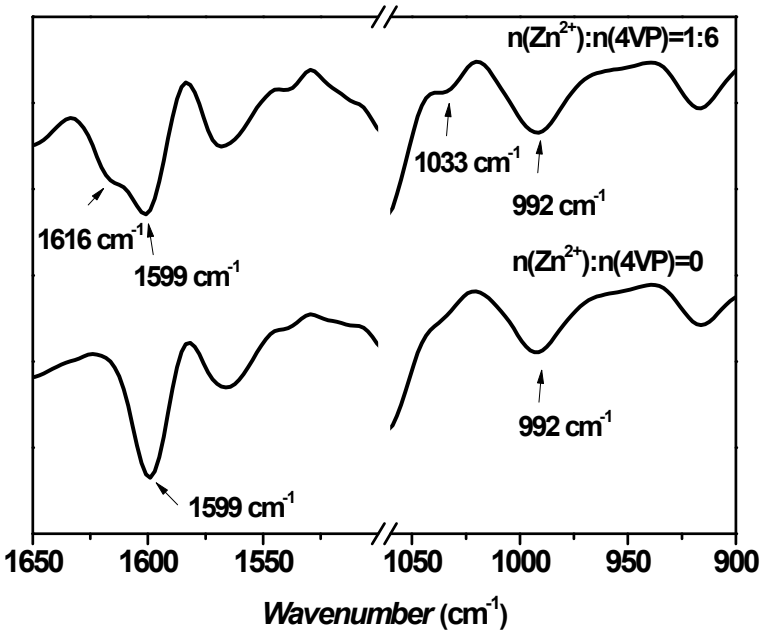

Fig. SI-8 FTIR spectra recorded in the region 1630-1500 cm^{-1} and 1060-900 cm^{-1} for the pure triblock $V_{30}H_{123}V_{30}$ and the triblock complexed with zinc perchlorate. $n(Zn^{2+}):n(4VP)$ is the molar ratio of Zn^{2+} to the repeating unit of 4VP.