Electronic Supplementary Material (ESI) for Polymer Chemistry.

Pyrene Label Used as a Scale for Sequence-Controlled Functionalized Polymers

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Characteristics of monomers

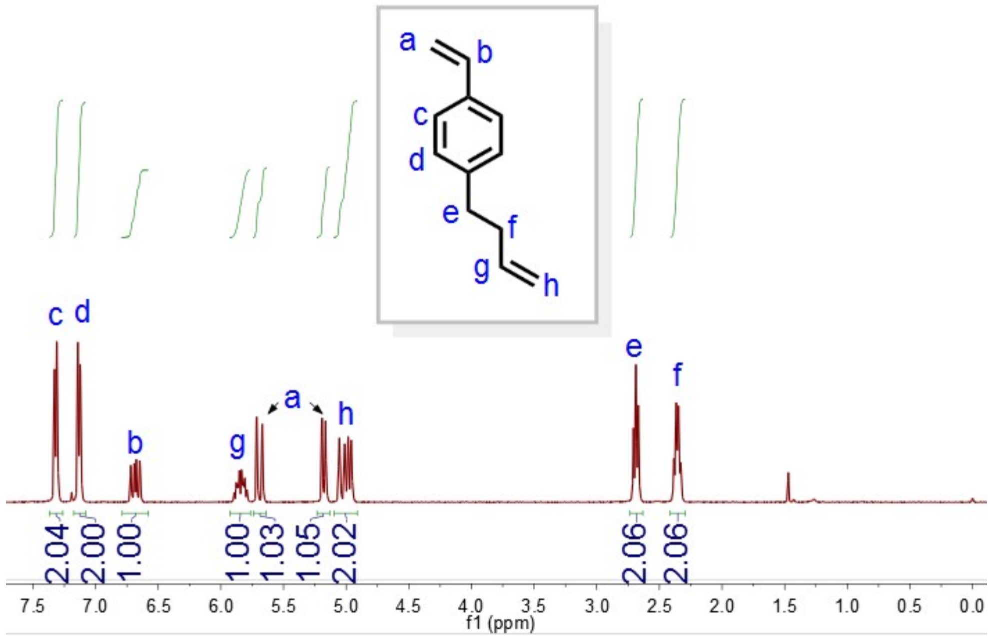

Figure S1 ^{1}H NMR of VSt.

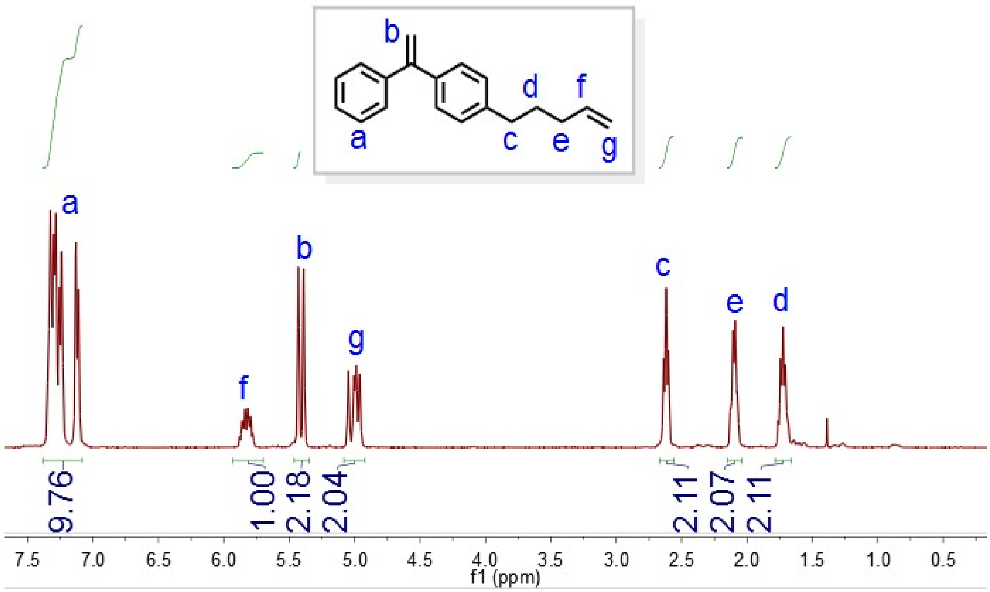

Figure S2 ^{1}H NMR of DPE-ene.

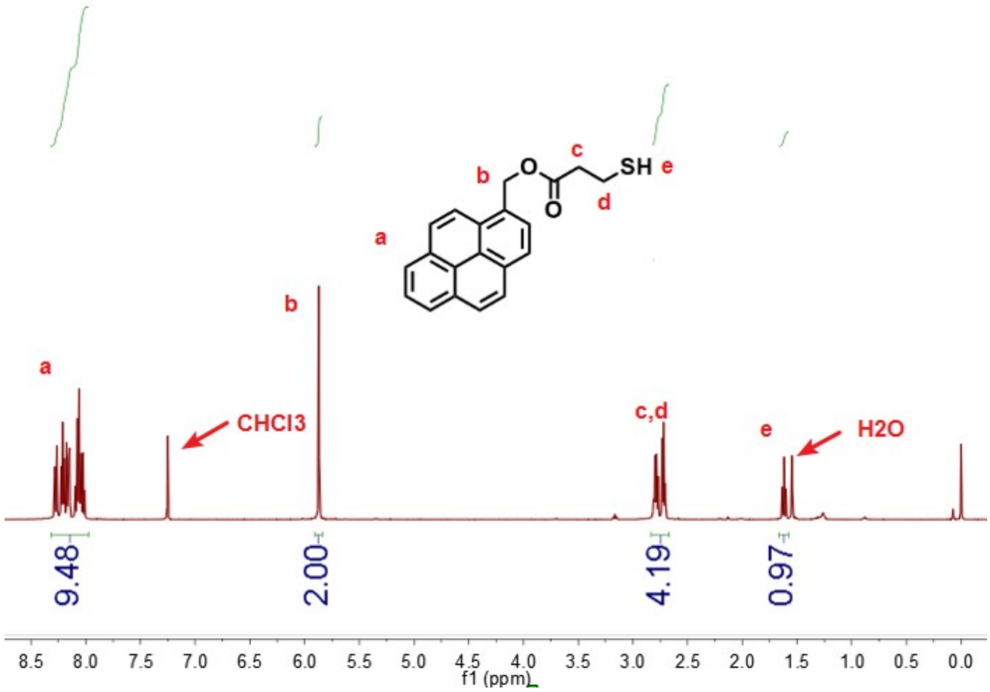

Figure S3 ^{1}H NMR of Py-SH.

Synthetic routes and characteristics of polymers

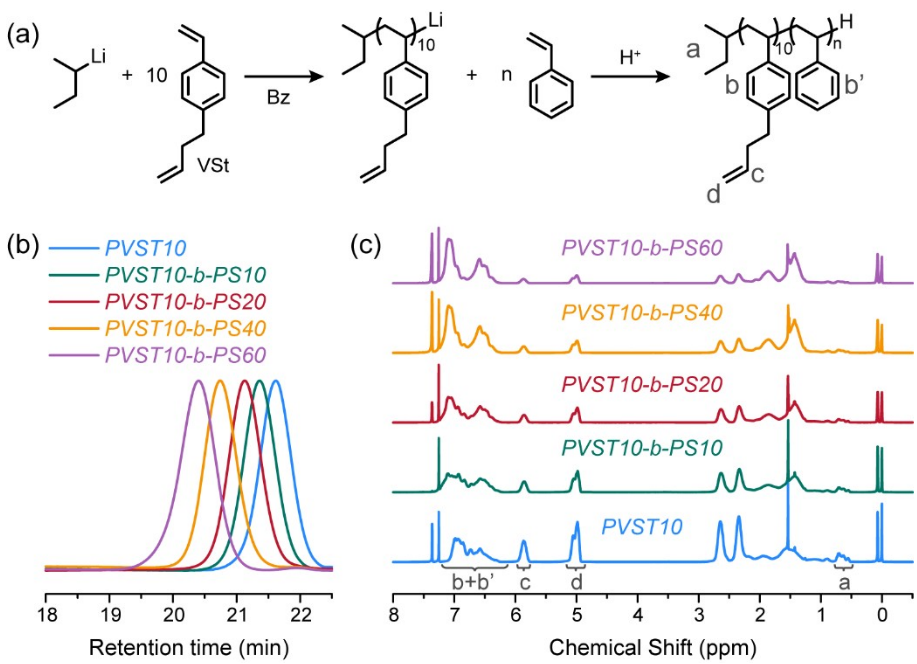

Figure S4 (a) Synthetic route of PVSt-*b*-PS block polymers. (b) SEC curves of PVSt-*b*-PS block polymers. (c) ^{1}H NMR spectra of PVSt-*b*-PS block polymers. The DP of VSt could be deduced using the equation: DP(VSt) = [Area(d)/2]/[(Area(a)/6]=10. The ratio of average number per chain of St to VSt (*N(St)/N(VSt)*) could be calculated using the equation: *N(St)/N(VSt)*=[Area(b+b')-4Area(c)]/5Area(c).

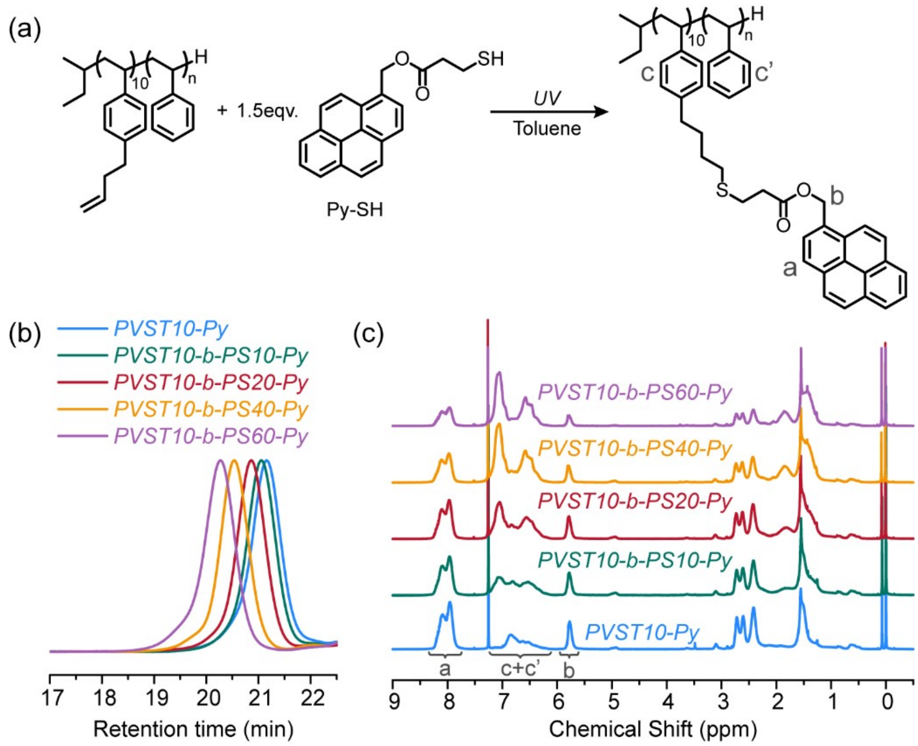

Figure S5 (a) Synthetic route of Py-labeled block polymers (PVSt-*b*-PS-Pys). (b) SEC curves of PVSt-*b*-PS-Pys. (c) ^{1}H NMR spectra of PVSt-*b*-PS-Pys. The grafting efficiency of Py-SH could be calculated using the equation:
E(x)= 4Area(a)/9[Area(c+c')*10*4/(10*4+x*5)], where, x is *N(St)*.

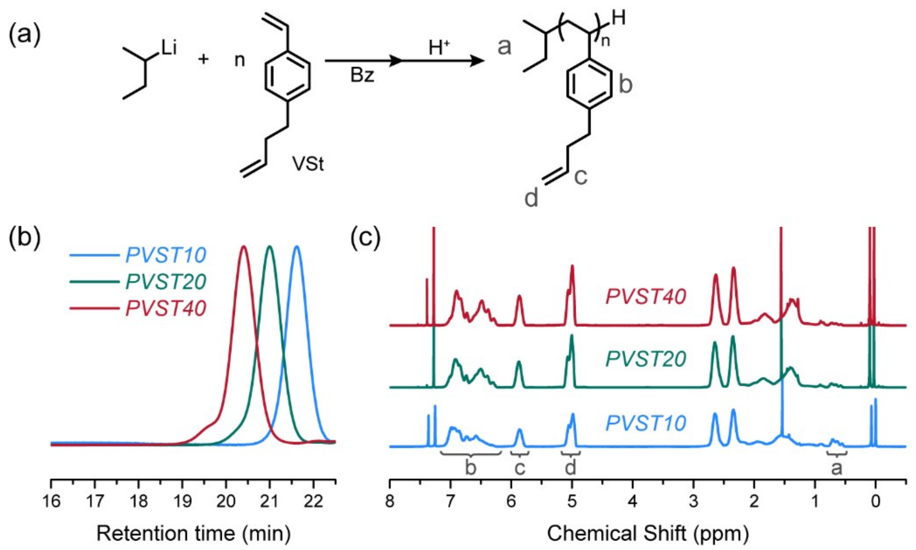

Figure S6 (a) Synthetic route of PVSt with different degree of polymerization (DP). (b) SEC curves of PVSts. (c) ^{1}H NMR spectra of PVSts. The DP could be calculated using the equation: DP = [Area(d)/2]/[(Area(a)/6].

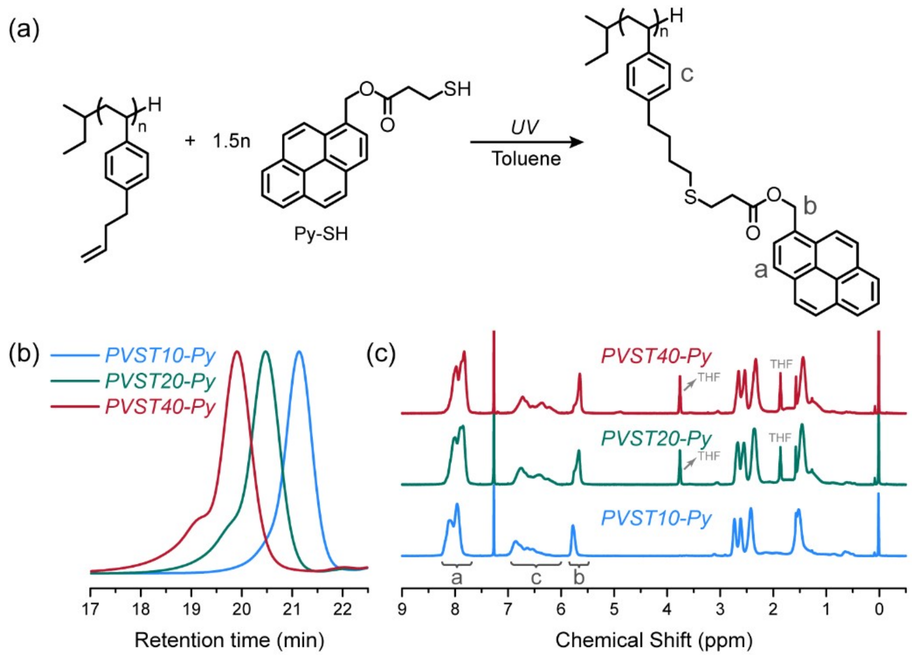

Figure S7 (a) Synthetic route of Py-labeled homopolymers (PVSt-Pys). (b) SEC curves of PVSt-Pys. (c) ^{1}H NMR spectra of PVSt-Pys. The grafting efficiency of Py-SH could be calculated using the equation: E = [Area(a)/9]/[(Area(c)/4].

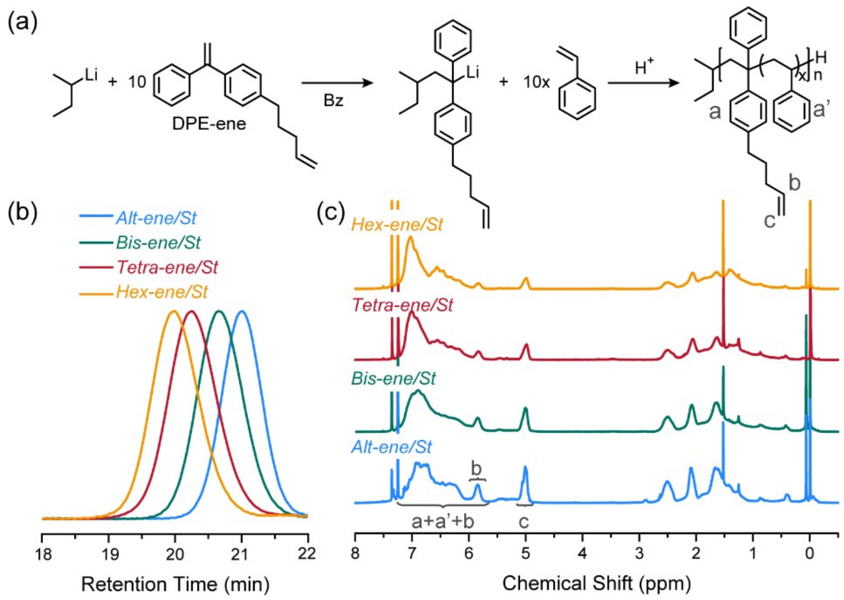

Figure S8 Synthetic route of copolymers of DPE-ene and St (ene/St) under [DPE-ene]$_0$/[St]$_0$ = 1.5:1, 1;2, 1:4 and 1:6. (b) SEC curves of ene/St copolymers. (c) ^{1}H NMR spectra of ene/St copolymers. The ratio of average number per chain of St to DPE-ene (*N(St)/N(DPE-ene)*) could be calculated using the equation:
N(St)/N(DPE-ene)=[2Area(a+a'+b)-10Area(c)]/5Area(c).

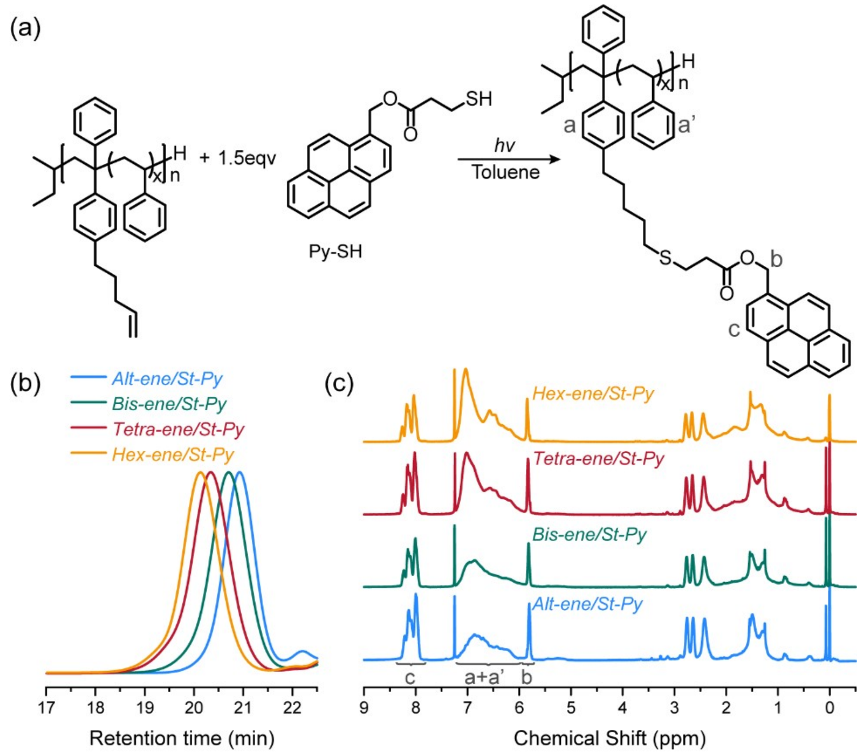

Figure S9 (a) Synthetic route of Py-labeled sequence-controlled polymers (ene/St-Pys). (b) SEC curves of ene/St-Pys. (c) ^{1}H NMR spectra of ene/St-Pys. The grafting efficiency of Py-SH could be calculated using the equation:

E(x) = Area(c)/[(Area(a+a'+b)-Area(b))*9/(5*x+9))], where, x is *N(St)/N(DPE-ene)*.

Relationship between pyrenyl concentration and UV absorbance

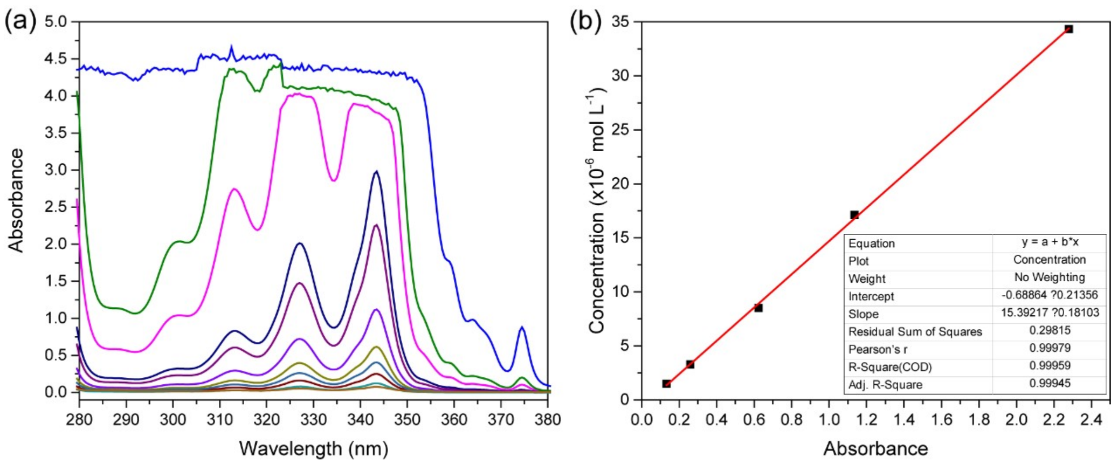

Figure S10 (a) Ultraviolet-visible absorption curves of 3-mercaptopropanoate-oxymethyl pyrene (Py-SH) under different concentration. (b) The linear relationship between pyrenyl concentration and absorbance (determined at 343 nm).

Molecular dynamics simulations

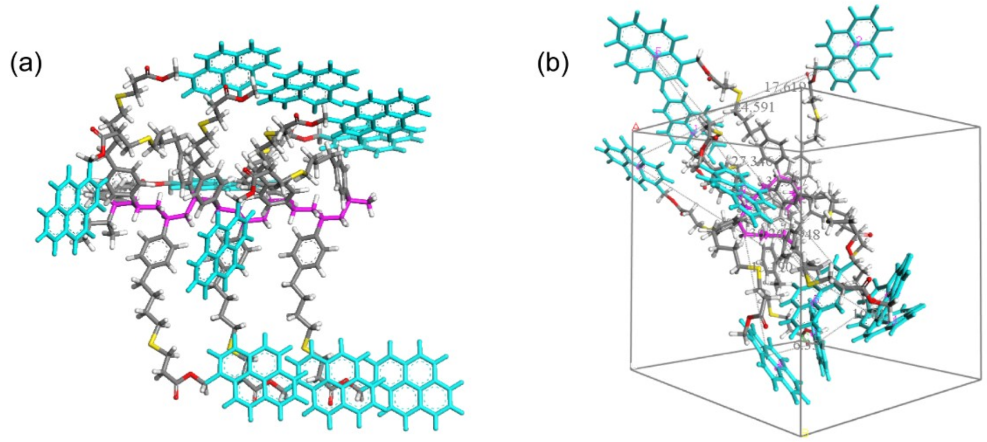

Figure S11 (a) Molecular models of *Uni*-PVSt-Py copolymer. (b) One of stable structures with relatively low energy after anneal simulation.

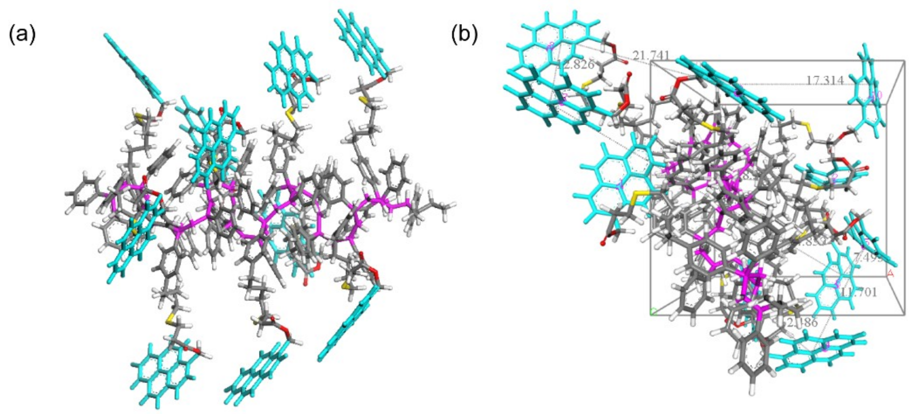

Figure S12 (a) Molecular models with uniform spaces of *Alt*-ene/St-Py copolymer. (b) One of stable structures with relatively low energy after anneal simulation.

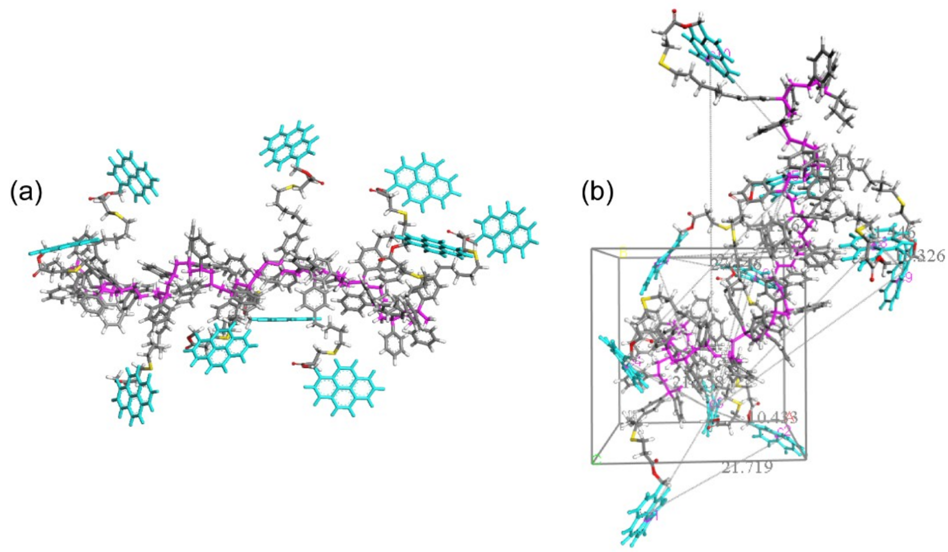

Figure S13 (a) Molecular models with uniform spaces of *Bis*-ene/St-Py copolymer. (b) One of stable structures with relatively low energy after anneal simulation.

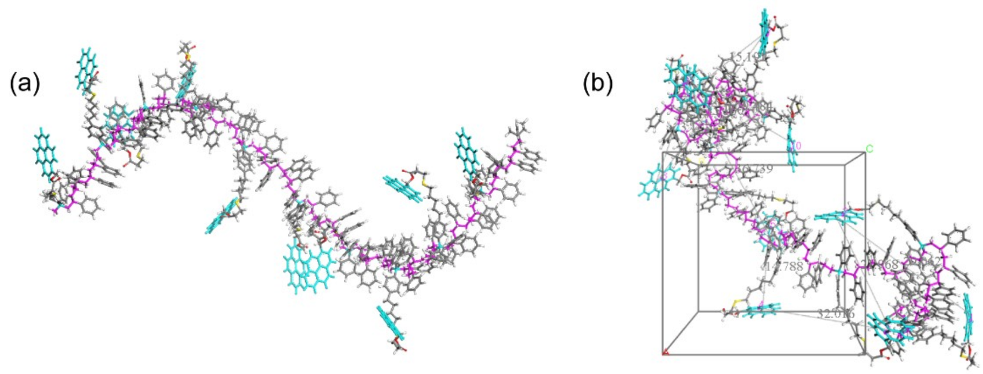

Figure S14 (a) Molecular models with uniform spaces of *Hex*-ene/St-Py copolymer. (b) One of stable structures with relatively low energy after anneal simulation.