Supporting Information

for

Cyclic Thioanhydride/Episulfide Copolymerizations by Bipyridine-Bisphenolate Aluminum/Onium Pair: Approach to Structurally and Functionally Diverse Poly(thioester)s

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Table S1. The copolymerization of CTAH and PS at different CTA equivalents.

Entry ^a	CTA/Cat.	T(℃)	<i>t</i> (min)	$\operatorname{Conv.}(\%)^b$	$M_{\rm n,theo}({\rm kDa})^c$	$M_{\rm n}({\rm kDa})^d$	D^d
1	5	25	50	94.1	5.9	13.9	1.20
2	10	25	25	85.5	2.7	6.2	1.16
3	20	25	30	83.0	1.3	3.0	1.16
4	50	25	30	97.4	0.6	1.2	1.20
5	100	25	30	74.8	0.2	0.7	1.24

 $s + \frac{s}{BnSH} + \frac{4/PPNCI}{BnSH} + \frac{s}{s}$

^{*a*} Unless other stated, the polymerizations were conducted in bulk at 25 °C, [PS]:[CTA]:[Lewis acid]:[Lewis base] = 1000/250/1/1. ^{*b*} Conversion of CTAH was determined by ¹H NMR. ^{*c*} The theoretical molecular weight was calculated based on the assumption that each Al center initiated two polymer chains. $M_{n,theo} = [M_{CTAH} + M_{PS}] \times 250 \times \text{conv}$ (%) × 0.5÷CTA/Cat. ^{*d*} Number-averaged molecular weight (M_n) and polydispersity (D) were determined by GPC and referenced by polystyrene standards. The $M_{n, GPC}$ was not corrected.



Figure S1. Kinetic plots of the copolymerization of CTAH and PS in toluene at 25 °C (Conditions: CTAH:PS:4:PPNCl = 250:250:1:1 in toluene, [PS] = 2.5 mol/L).



Figure S2. Kinetic plots of the copolymerization of CTAH and PS at 25 °C and 40 °C.



Figure S3. The copolymer obtained by copolymerization of CTAH and PS at 40 °C.



Figure S4. The relationship between CTA/Cat. and M_n .



Figure S5. ¹H NMR spectrum of 8-menmbered cyclic molecules in DMSO.



Figure S6. Kinetics of CTAH/PS copolymerisation with CTAH/CHS.



Figure S7. DSC thermogram of the poly(STAH-*alt*-PS).



Figure S8. DSC thermogram of the poly(GTAH-*alt*-PS).



Figure S9. DSC thermogram of the poly(CTAH-alt-PS).



Figure S10. DSC thermogram of the poly(CTAH-alt-CHS).



Figure S11. TGA curve of poly(CTAH-alt-PS).



Figure S12. TGA curve of poly(CTAH-*alt*-CHS).



Figure S13. The TG-IR analysis of the poly(CTAH-alt-PS).



Figure S14. The FT-IR analysis of the poly(CTAH-*alt*-PS) and crosslinked polymer.



Figure S15. DSC thermogram of the polymer crosslinked by BDT.



Figure S16. DSC thermogram of the polymer crosslinked by TBT.



Figure S17. The GPC elution curves of the block polythioester.



Figure S18. DOSY NMR spectrum of the polymer blends.



Figure A1. ¹H NMR spectrum of poly(STAH-alt-PS) in CDCl₃.



Figure A2. ¹³C NMR spectrum of poly(STAH-alt-PS) in CDCl₃.



Figure A3. ¹H NMR spectrum of poly(STAH-alt-CHS) in CDCl₃.



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Figure A6. ¹³C NMR spectrum of poly(GTAH-alt-PS) in CDCl₃.



Figure A7. ¹H NMR spectrum of poly(GTAH-alt-CHS) in CDCl₃.



Figure A8. ¹³C NMR spectrum of poly(GTAH-alt-CHS) in CDCl₃.



Figure A9. ¹H NMR spectrum of poly(CTAH-*alt*-PS) in CDCl₃.



Figure A10. ¹³C NMR spectrum of poly(CTAH-alt-PS) in CDCl₃.



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Figure A12. ¹³C NMR spectrum of poly(CTAH-alt-CHS) in CDCl₃.



Figure A13. ¹H NMR spectrum of poly(CHTH-alt-PS) in CDCl₃.



Figure A14. ¹³C NMR spectrum of poly(CHTH-alt-PS) in CDCl₃.



Figure A15. ¹H NMR spectrum of poly(CHTH-alt-CHS) in CDCl₃.



Figure A16. ¹³C NMR Spectrum of poly(CHTH-alt-CHS) in CDCl₃.



Figure A17. DSC thermogram of the poly(STAH-alt-CHS).



Figure A18. DSC thermogram of the poly(GTAH-*alt*-CHS).



Figure A19. DSC thermogram of the poly(CHTH-alt-PS).



Figure A20. DSC thermogram of the poly(CHTH-alt-CHS).



Figure A21. TGA curve of poly(STAH-alt-PS).



Figure A22. TGA curve of poly(STAH-*alt*-CHS).



Figure A23. TGA curve of poly(GTAH-*alt*-PS).



Figure A24. TGA curve of poly(GTAH-alt-CHS).



Figure A25. TGA curve of poly(CHTH-alt-PS).



Figure A26. TGA curve of poly(CHTH-alt-CHS).



Figure A27. ¹H NMR spectrum of block polythioester.



Figure A28. ¹³C NMR spectrum of block polythioester.