Electronic Supplementary Material (ESI) for Polymer Chemistry.
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Supporting Information

Polymer Chemistry

One-pot synthesis of structure-controlled temperature-responsive polymer gels

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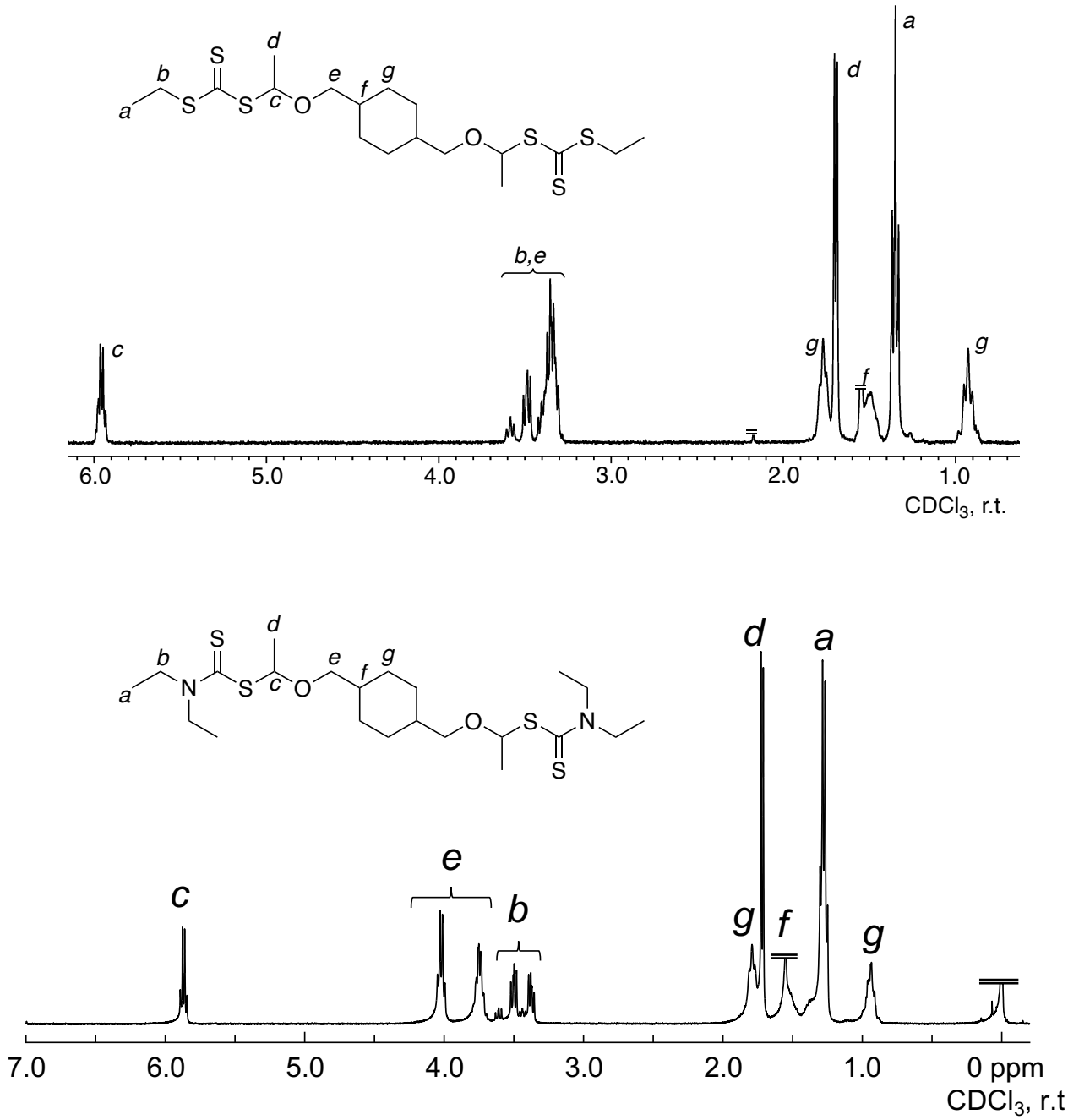


Figure S1. [1]H NMR spectra of difunctional RAFT agents DVE-TTC and DVE-DTC.

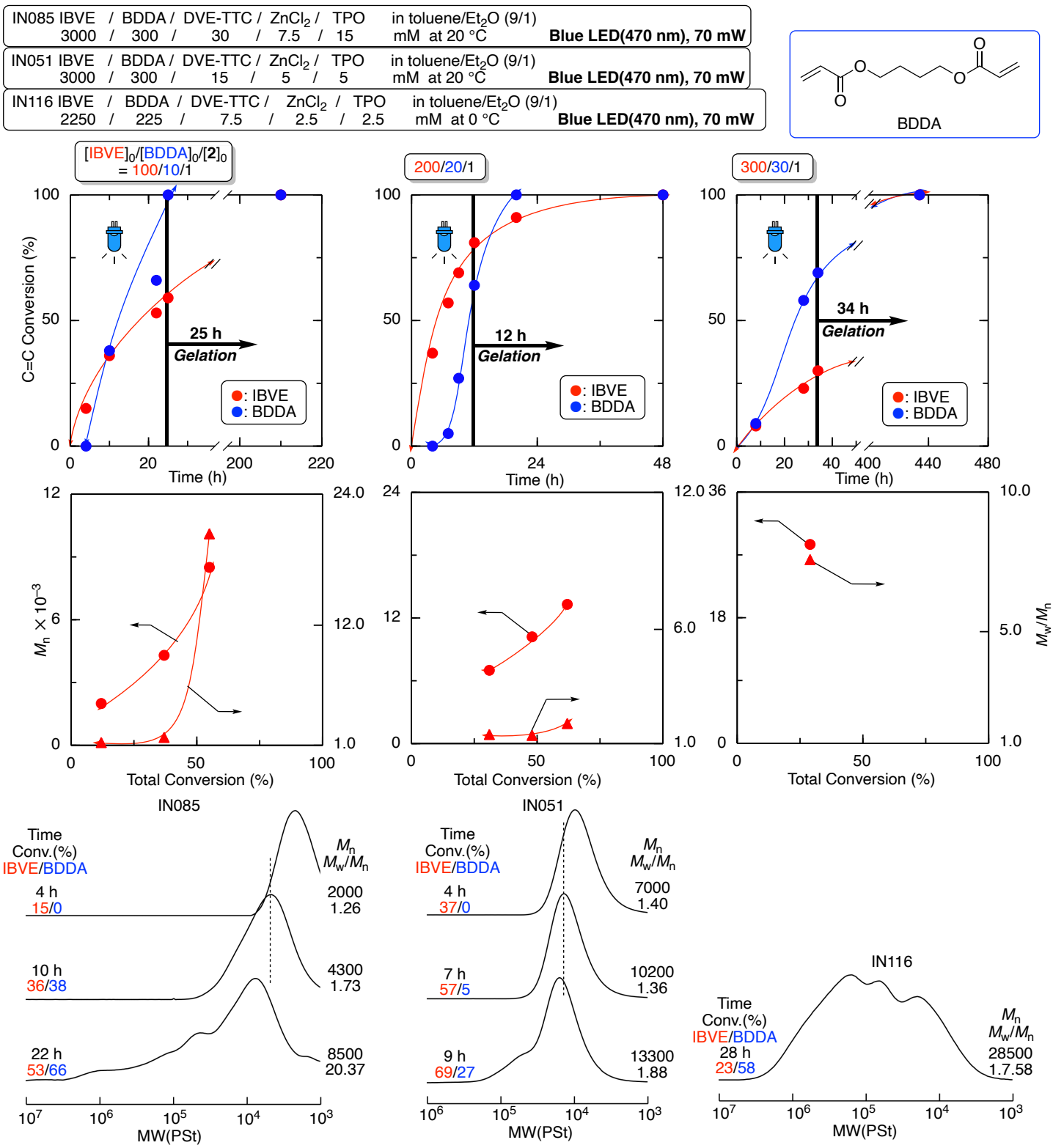
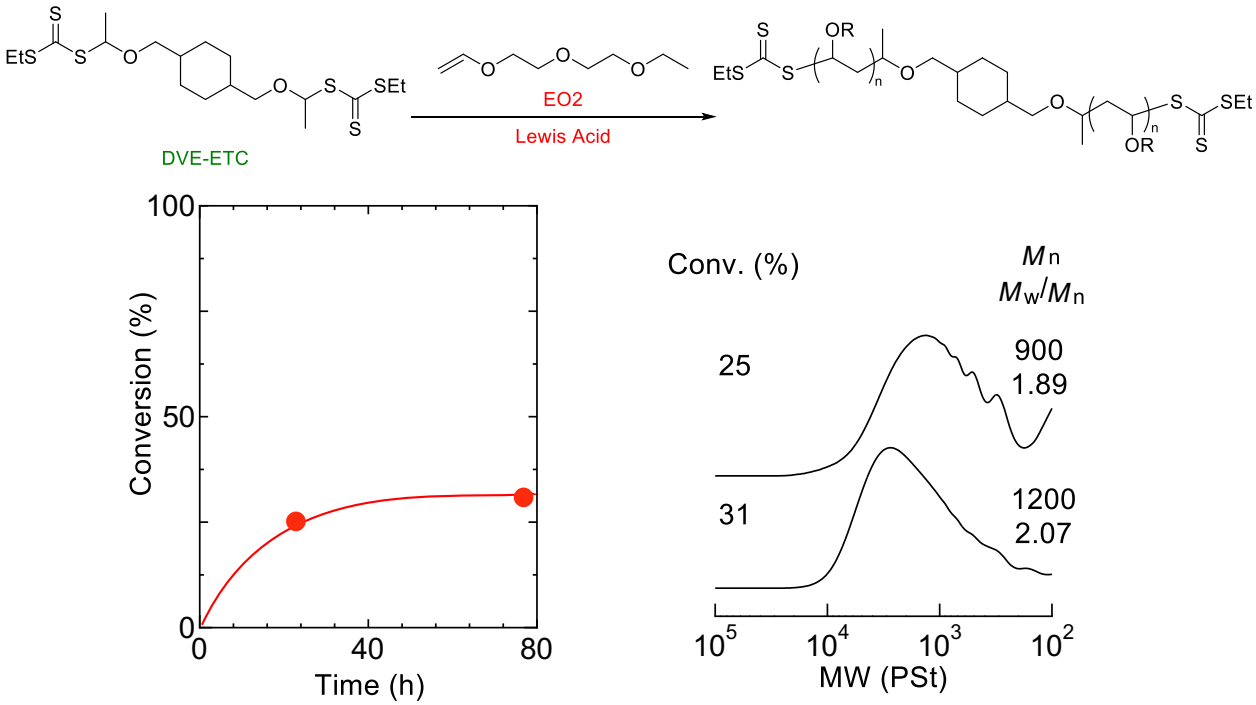
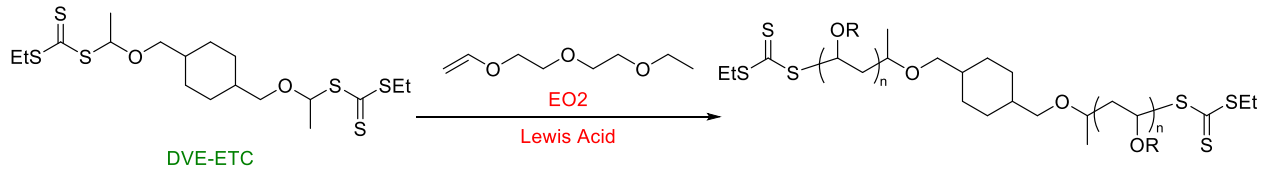


Figure S2. Polymerization of IBVE and BDDA with DVE-TTC/$ZnCl_2$/TPO just under LED irradiation as a control experiment.

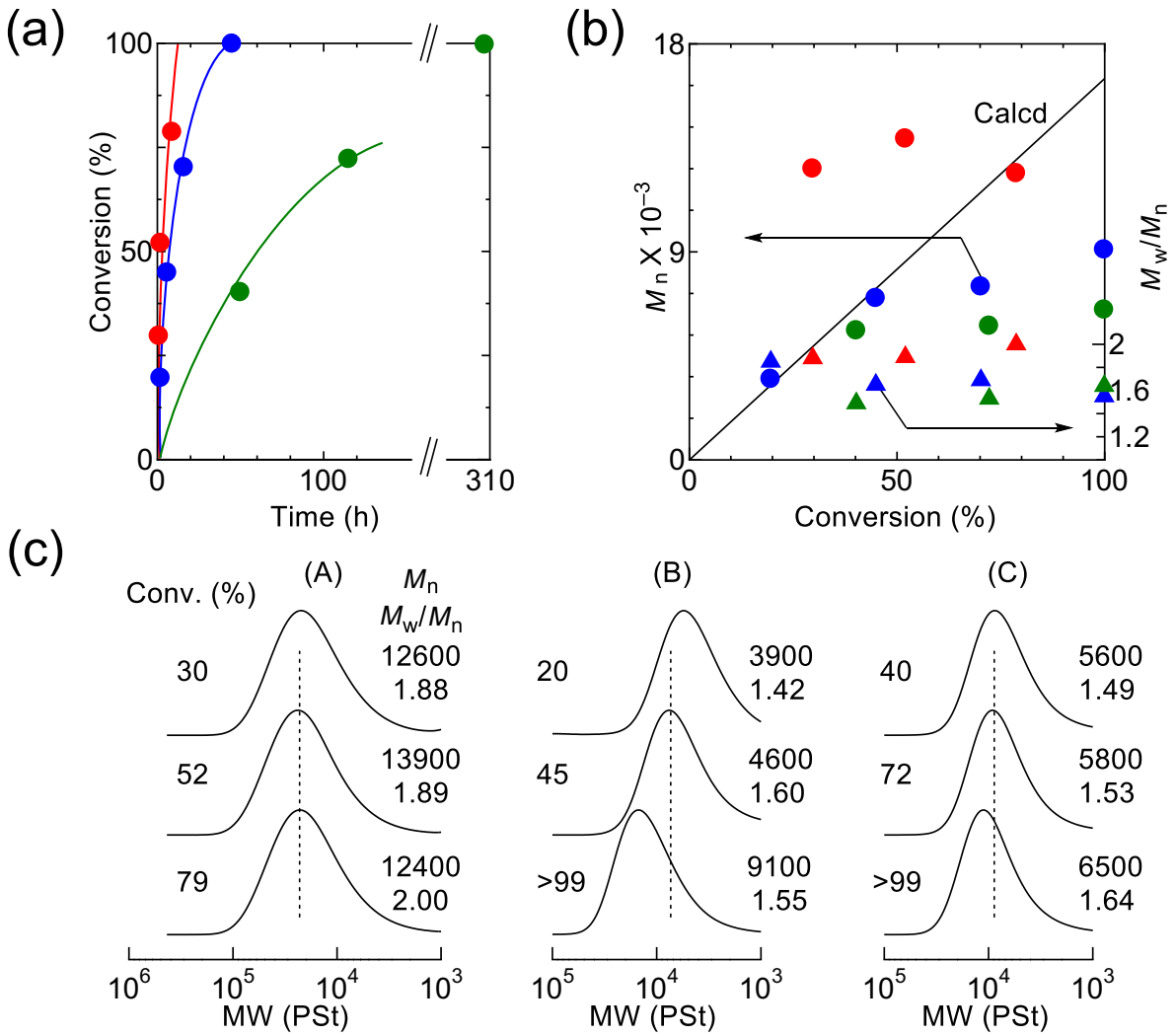


$[EO2]_0$ = 1.0 M, $[RAFT\ Agent]_0$ = 10 mM, $[ZnCl_2]_0$ = 40 mM, in toluene/Et_2O (9/1) at 0 °C.

Figure S3. Cationic polymerization with $ZnCl_2$.

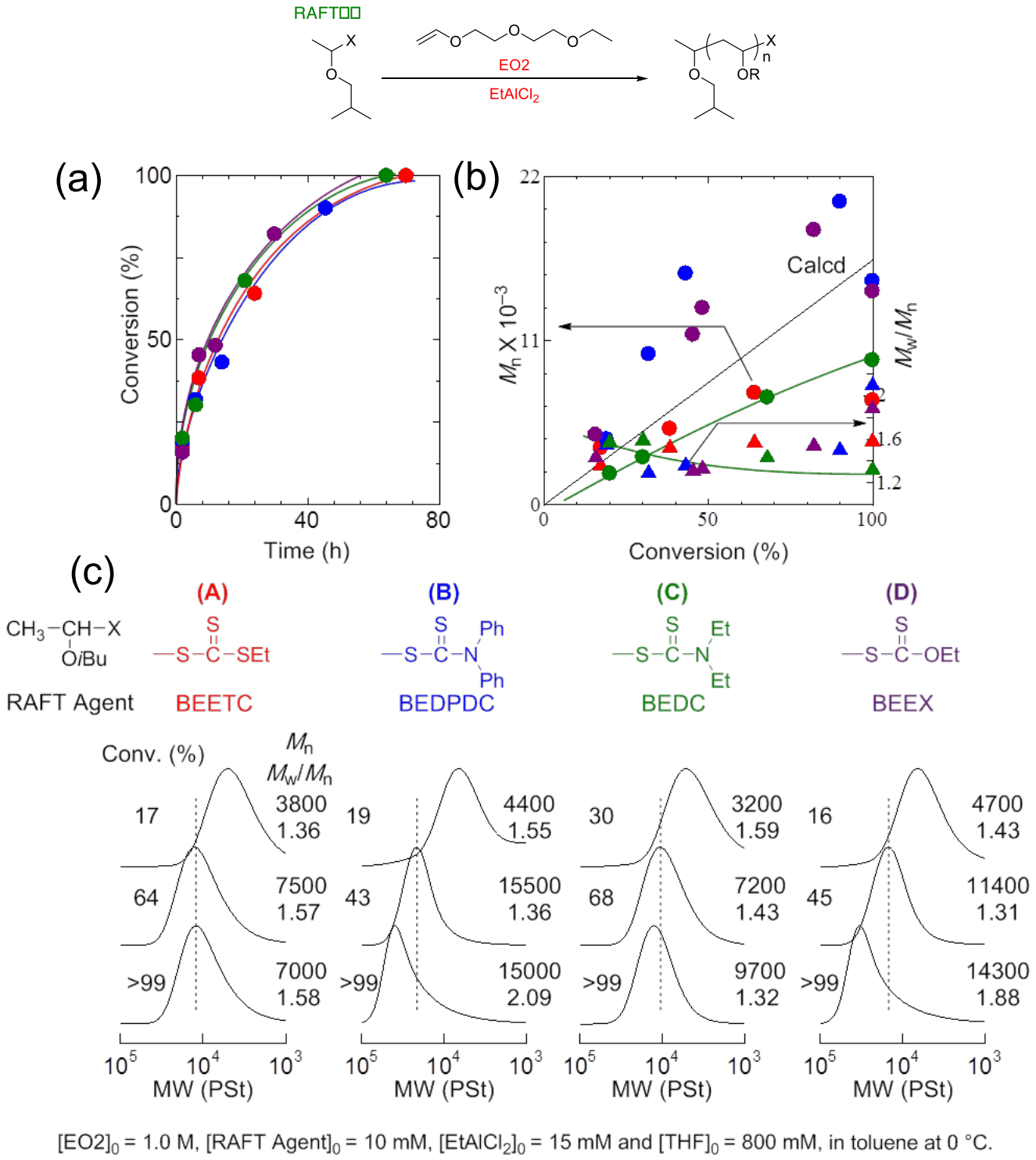


●, ▲ : (A) Without added base at −40 °C
●, ▲ : (B) [THF] = 800 mM at 0 °C
●, ▲ : (C) [THF] = 800 mM at −30 °C



(A) $[EO2]_0$ = 1.0 M, $[DVE\text{-}ETC]_0$ = 10 mM and $[EtAlCl_2]_0$ = 15 mM, in toluene at –40 °C.
(B)(C) $[EO2]_0$ = 1.0 M, $[DVE\text{-}ETC]_0$ = 10 mM, $[EtAlCl_2]_0$ = 15 mM and [THF] = 800 mM, in toluene at 0°C or –30 °C.

Figure S4. Cationic polymerization with trithiocarbonate RAFT agent.



[EO2]$_0$ = 1.0 M, [RAFT Agent]$_0$ = 10 mM, [EtAlCl$_2$]$_0$ = 15 mM and [THF]$_0$ = 800 mM, in toluene at 0 °C.

Figure S5. Effect of various RAFT agents.

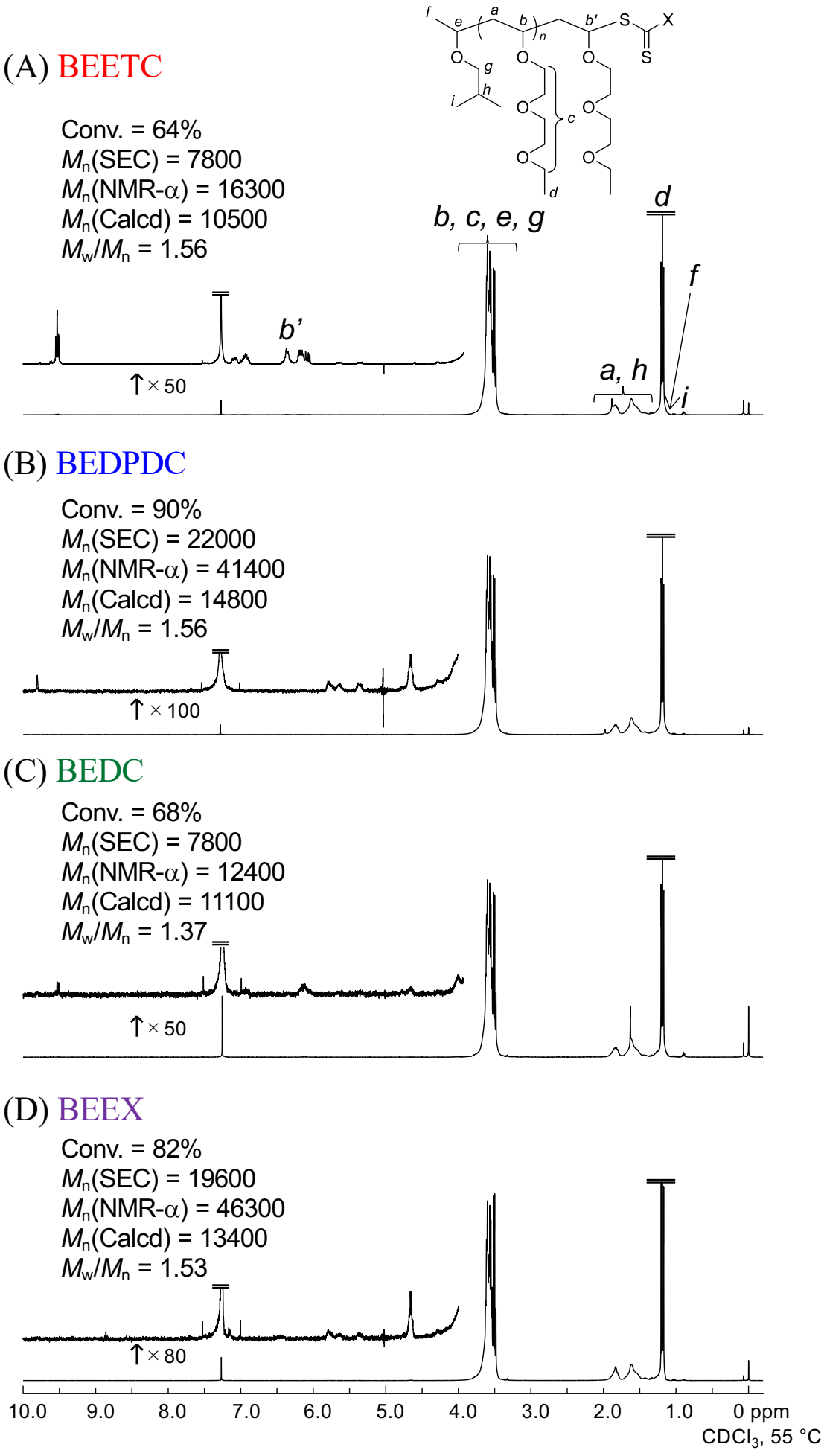
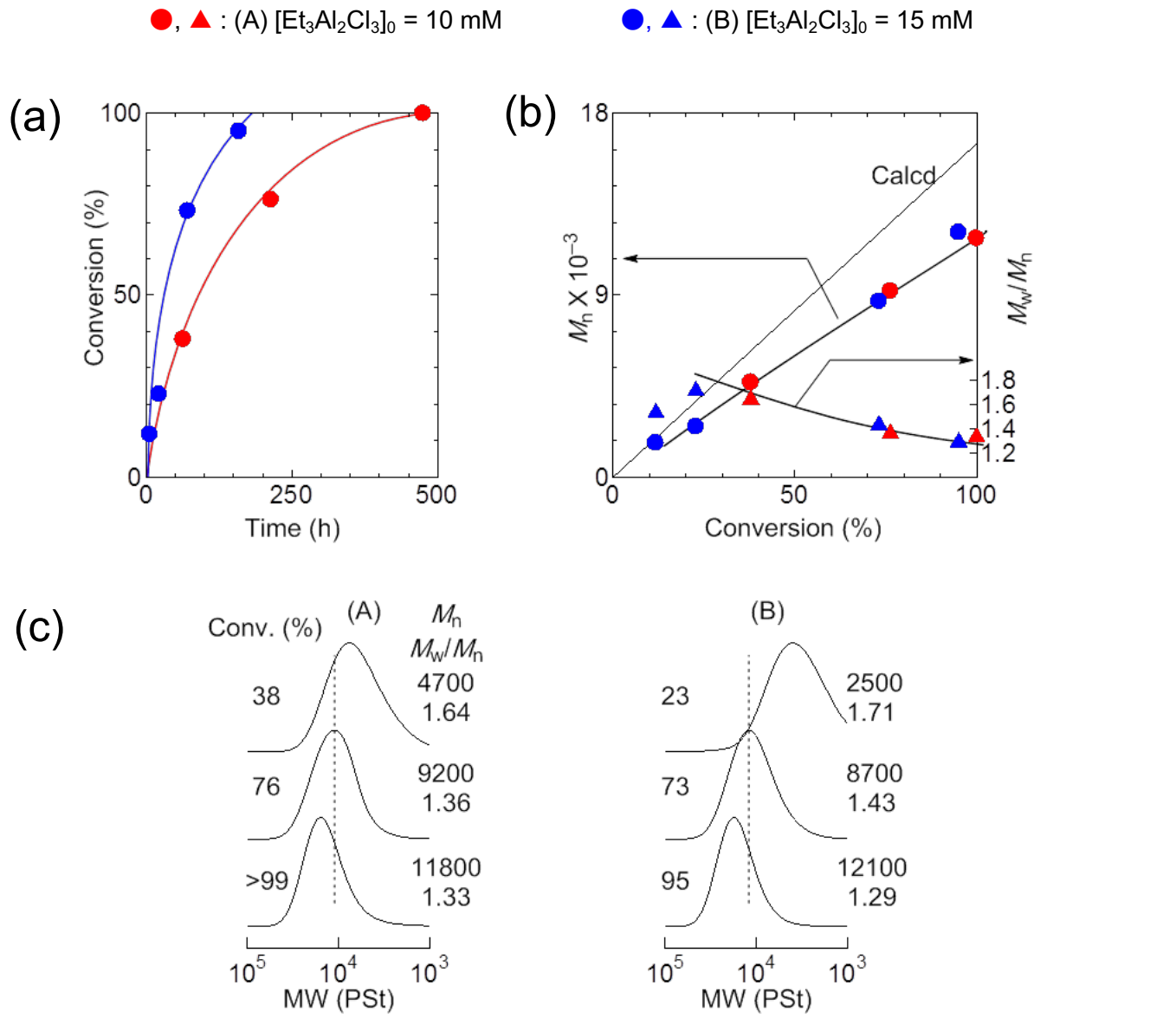
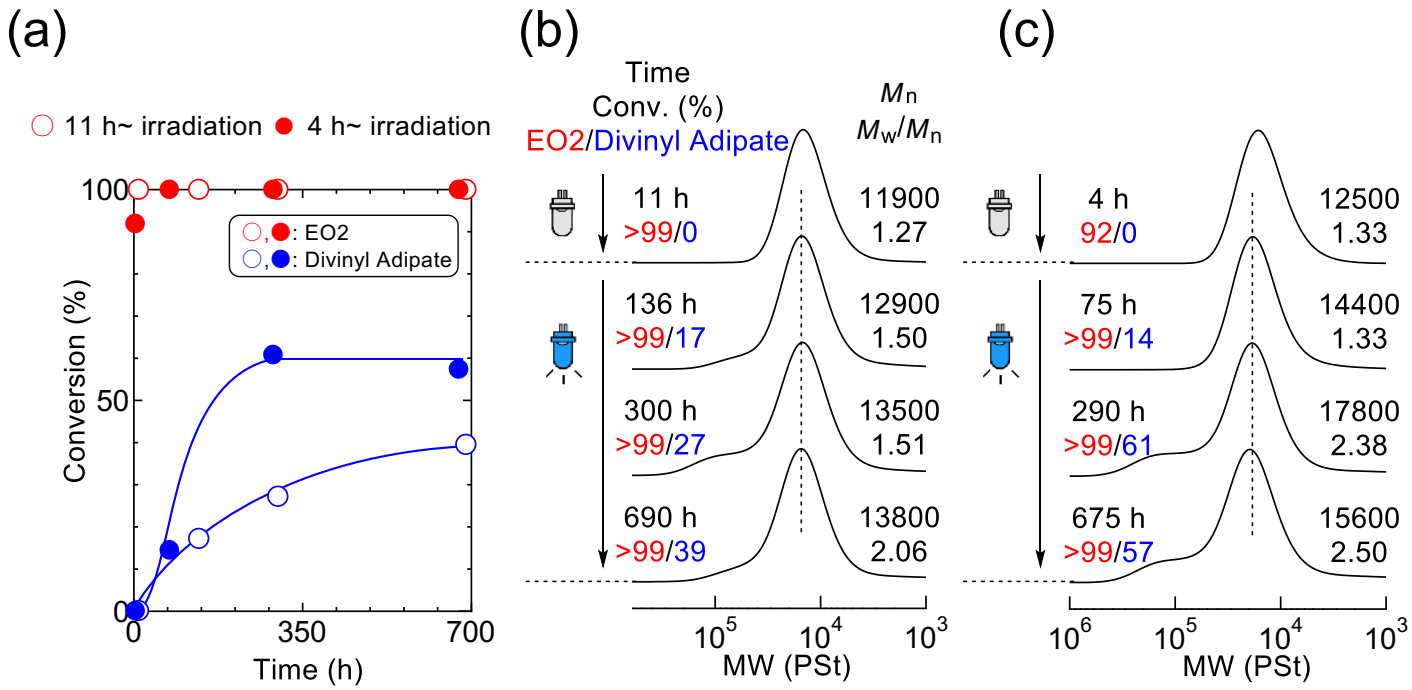


Figure S6. ^{1}H NMR spectra of PEO2 with various RAFT agents.



(A),(B) $[EO2]_0$ = 1.0 M, $[DVE\text{-}DC]_0$ = 10 mM, $[Et_3Al_2Cl_3]_0$ = 10 or 15 mM and [THF] = 400 mM, in toluene at 0 °C.

Figure S7. Cationic polymerization with another Lewis acid.



$[EO2]_0$ = 1.0 M, $[RAFT\ Agent]_0$ = 10 mM, $[Divinyl\ Adipate]_0$ = 200 mM,
[TPO] = 7 mM, $[Et_3Al_2Cl_3]$ = 15 mM and [EtOAc] = 1.0 M, in toluene at 4 °C.

Figure S8. Effect of irradiation start time of blue LED on this reaction system, polymerization was performed using 20 equivalents of cross-linker relative to initiator at an EO2 monomer concentration of 1.0 mol L^{-1}(denoted by *M* in Figure) (the ratio of initiator, monomer, and cross-linker preparation was 1:100:20)
(a) Reactivity of crosslinker when exposed to light after EO2 has completely reacted (open circles) or with 10% EO2 remaining (solid circles), (b) Time dependence of the SEC of the polymer obtained by light irradiation after EO2 has completely reacted, (c) Time dependence of SEC of polymer obtained by light irradiation with 10% EO2 remaining

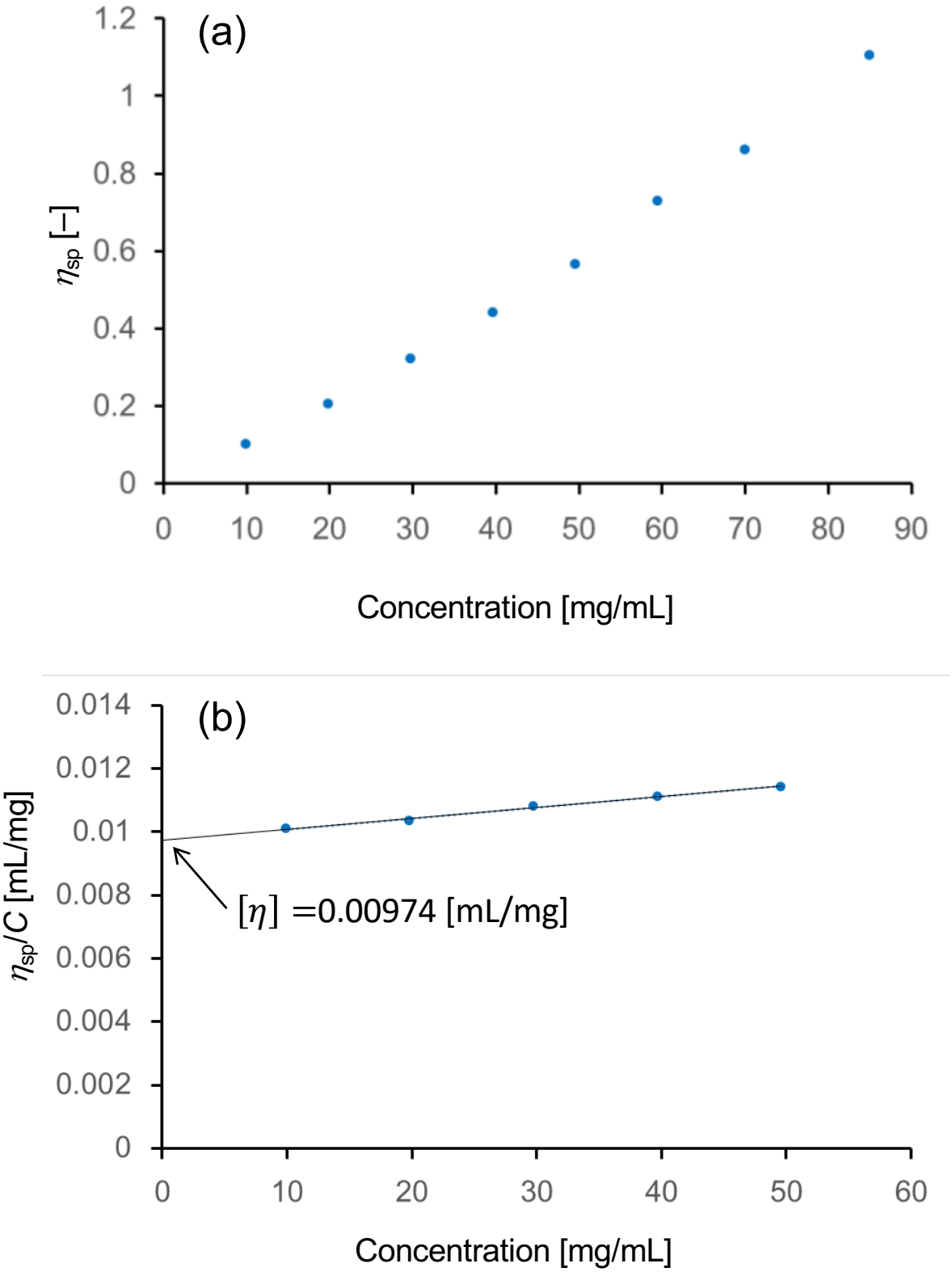


Figure S9. (a) Dependence of value of η_{sp} on concentration of 100-mer PEO2. (b) Plots of η_{sp}/C vs concentration of 100-mer PEO2.

(c)

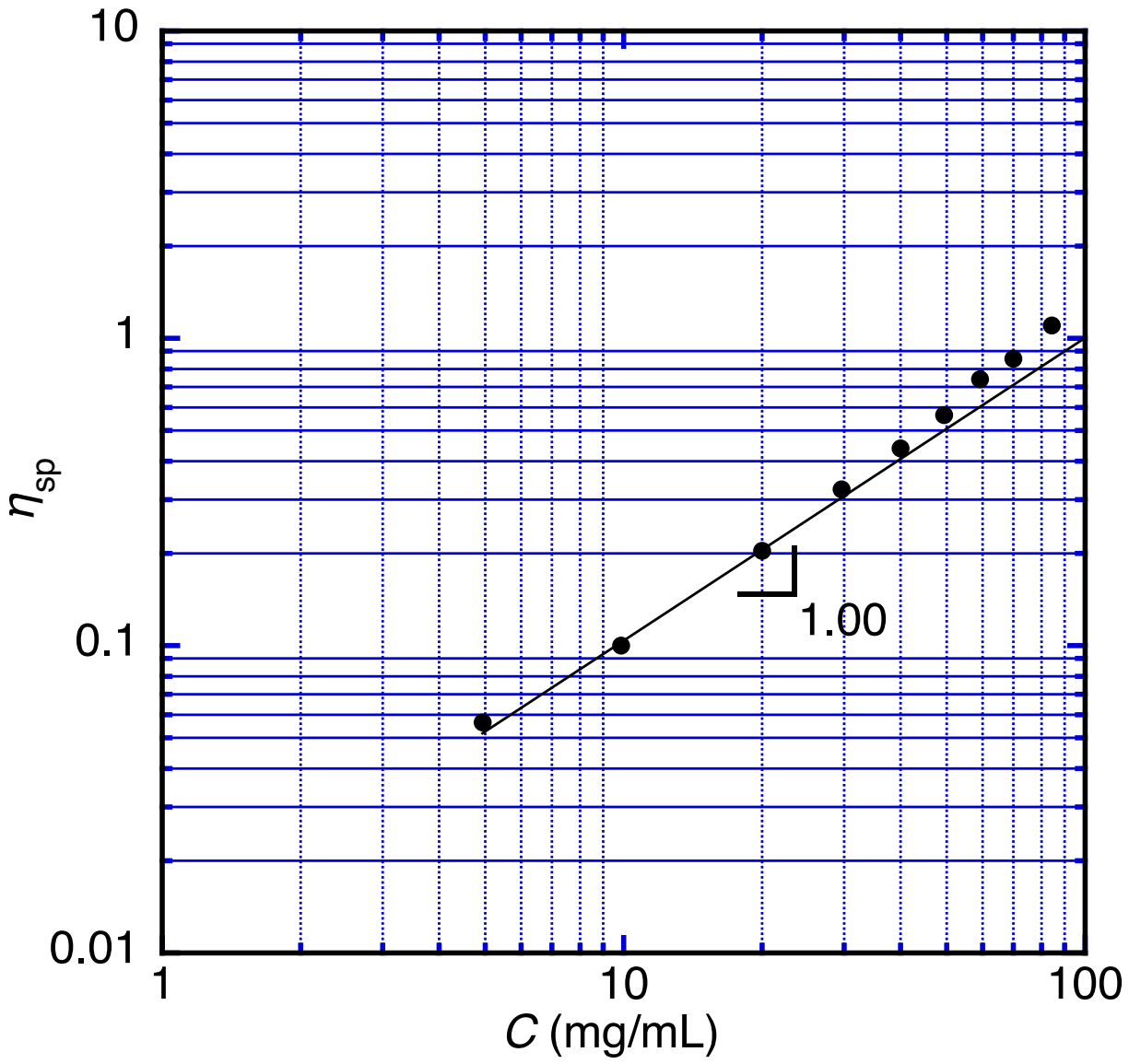


Figure S9. (c) Both log-log plots in Figure (a)
The slope of the log plot of reduced viscosity versus polymer concentration is 1, indicating that this solution is a dilute solution with no interactions between the polymers. When the slope approaches 2, the solution is semi-dilute and the macromolecules are packed together in a pressed state with no entanglement between the macromolecules. When the slope reaches 14/3, the polymers are entangled with each other.

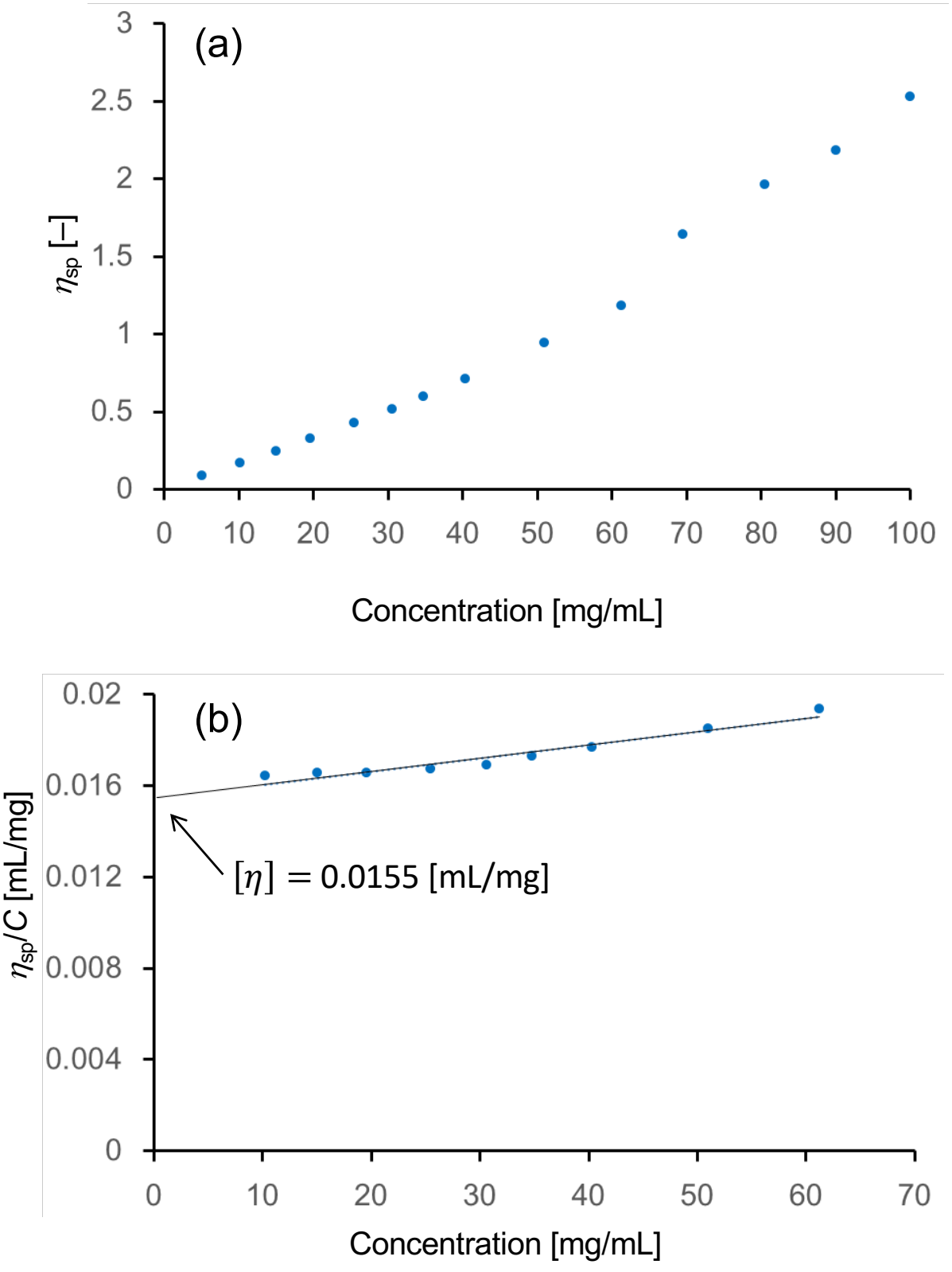


Figure S10. (a) Dependence of value of η_{sp} on concentration of 200arm PEO2. (b) Plots of η_{sp}/C vs concentration of 200-mer PEO2.

(c)

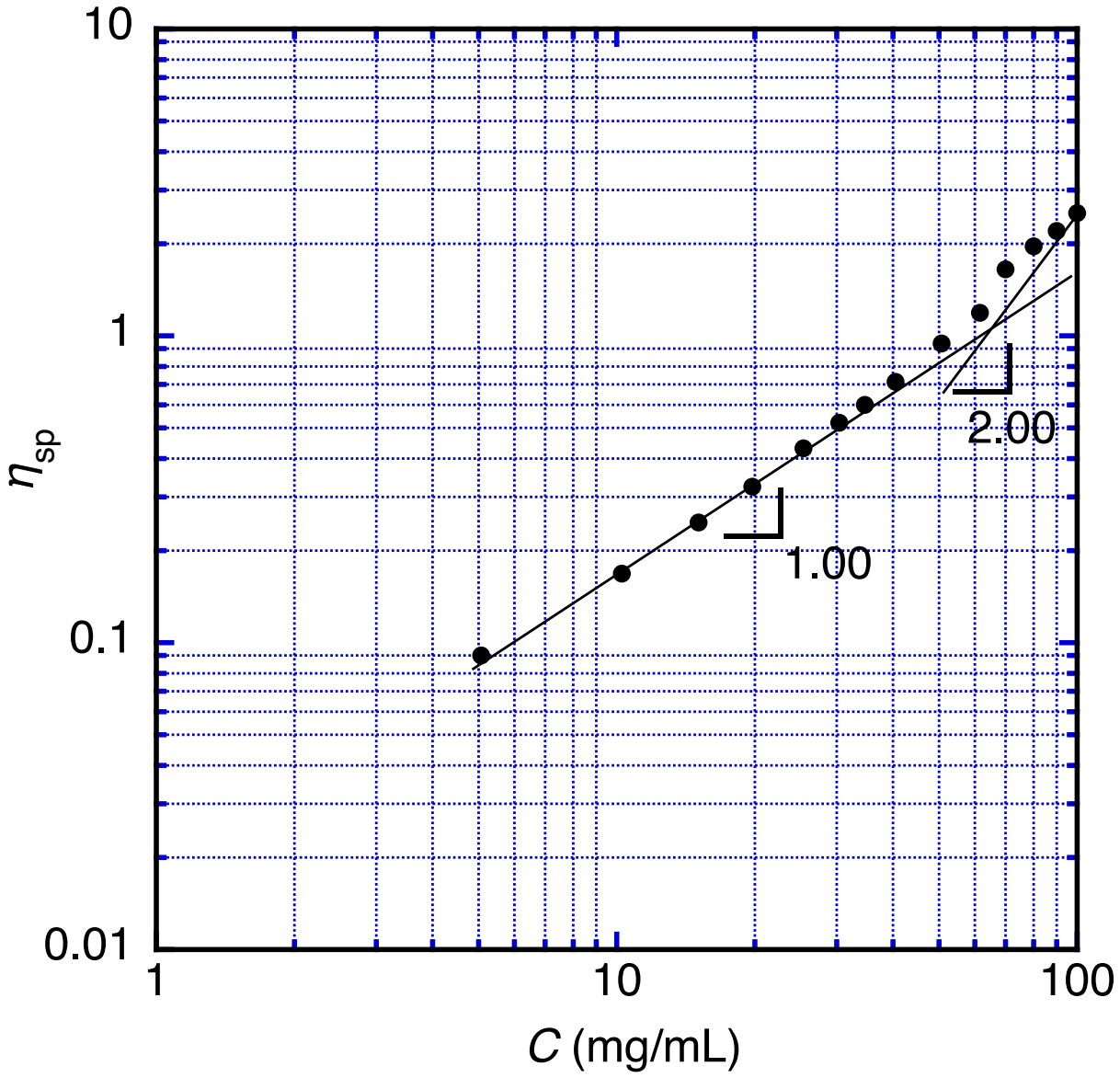
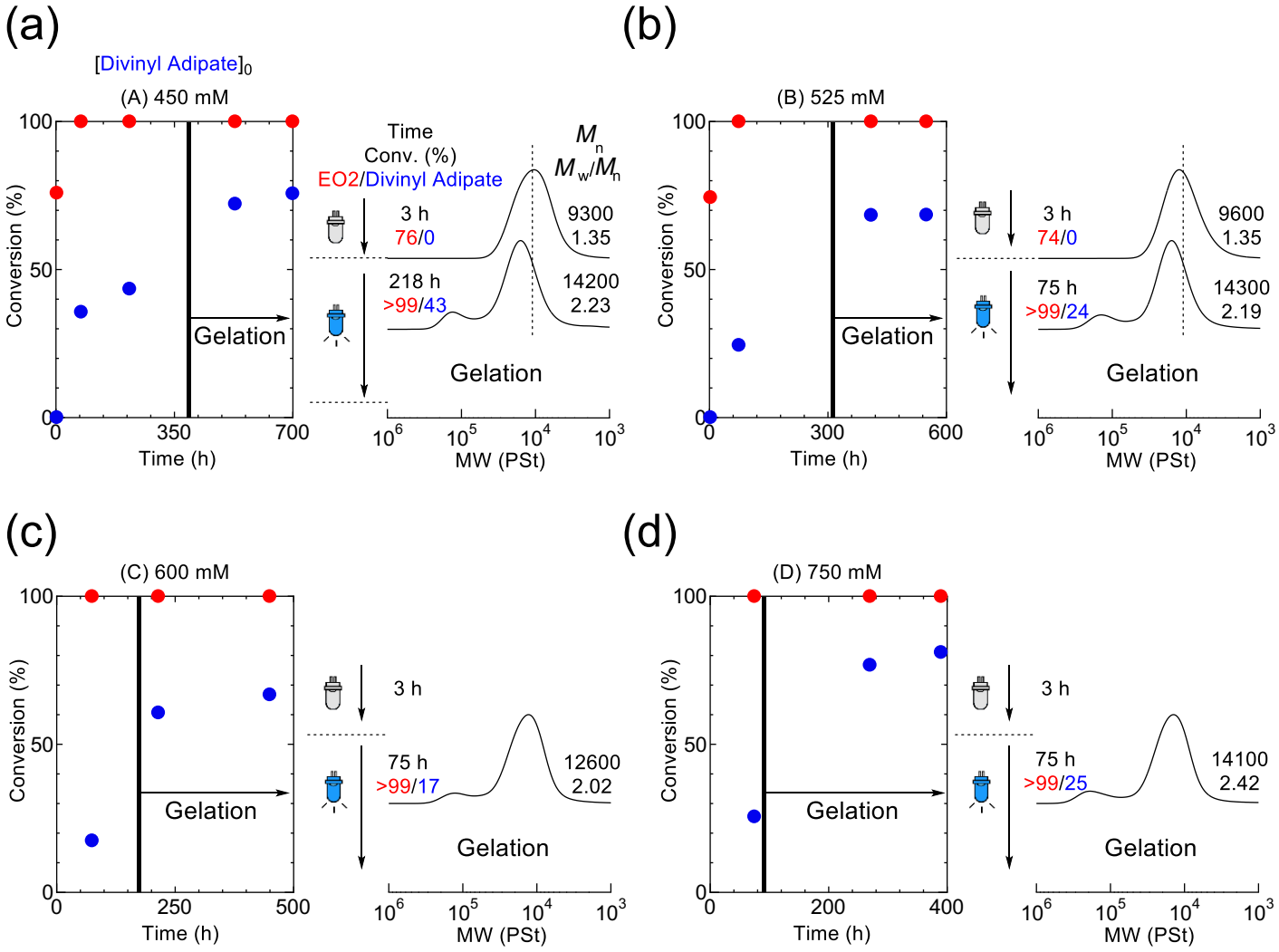


Figure S10. (c) Both log-log plots in Figure (a)
The slope of the log plot of reduced viscosity versus polymer concentration is 1, indicating that this solution is a dilute solution with no interactions between the polymers. When the slope approaches 2, the solution is semi-dilute and the macromolecules are packed together in a pressed state with no entanglement between the macromolecules. When the slope reaches 14/3, the polymers are entangled with each other.



$[EO2]_0$ = 1.5 M, $[RAFT\ Agent]_0$ = 15 mM, $[Divinyl\ Adipate]_0$ = 450—750 mM,
[TPO] = 5(B—D), 7(A) mM, $[Et_3Al_2Cl_3]$ = 15 mM and [EtOAc] = 1.0 M, in toluene at 4 °C.

(e)

[RAFT Agent] (mol L^{-1})	/	[EO2] (mol L^{-1})	/	[Divinyl Adipate]] (mol L^{-1})		
0.015	/	1.500	/	0.450	→	**GEL 400 h**
0.015	/	1.500	/	0.525	→	**GEL 310 h**
0.015	/	1.500	/	0.600	→	**GEL 170 h**
0.015	/	1.500	/	0.750	→	**GEL 90 h**

Figure S11. Effect of cross-linker concentration on gelation
(a) Time dependence of the reaction at a concentration of 450 mM of cross-linking agent (divinyl adipate), (b) Time dependence of the reaction at a concentration of 525 mM of cross-linking agent, (c) Time dependence of the reaction at a concentration of 600 mM of cross-linking agent, (d) Time dependence of the reaction at a concentration of 750 mM of cross-linking agent, (e) Gelation time obtained from (a)~(d)

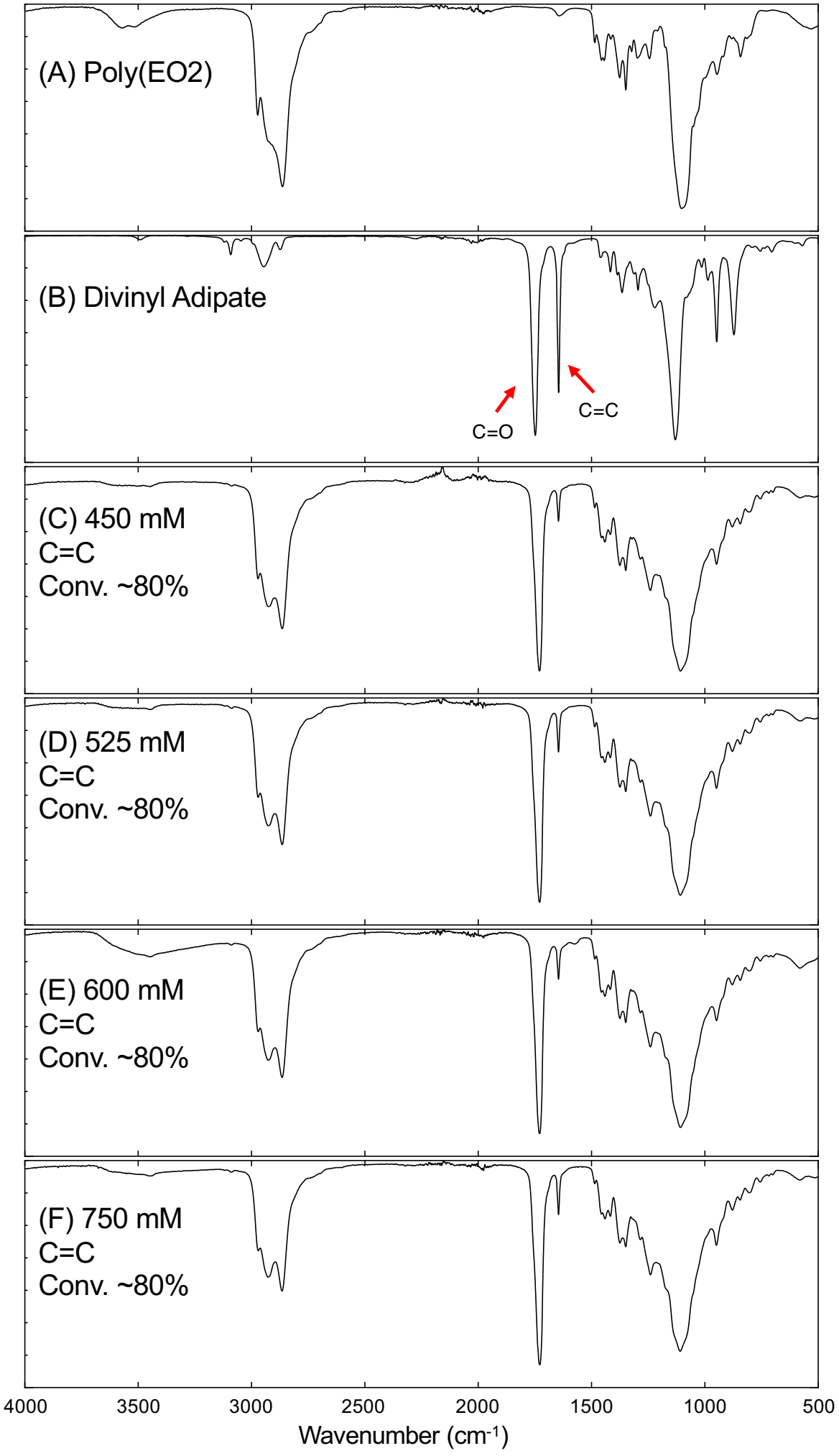


Figure S12. ATR-FTIR spectra of (A) PEO2, (B) Cross-linker, and (C–F) Gels obtained by adding different amounts of cross-linkers