10.1071/CH12152_AC

Australian Journal of Chemistry 2012, 65(8), 1077-1089

Supplementary Material for

Probing the RAFT Process Using a Model Reaction between Alkoxyamine and Dithioester

Changxi Li, Junpo He*, Ying Liu, Yanwu Zhou, Yuliang Yang

State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200433, China

Corresponding author: Junpo He; E-mail: jphe@fudan.edu.cn

The characterization results of RAFT agents

1. 2-Cyanoprop-2-yl dithiobenzoate (CNSS)

^{1}H NMR: δ (ppm): 1.95 (*s*, 6H, C***H*****$_3$**-C-C***H*****$_3$**), 7.92 (*d*, 2H, *o*-ArH), 7.56(*dd*, 1H, *p*-ArH), 7.40 (*dd*, 2H, *m*-ArH)**.** FT-IR: *v* (cm^{-1}) = 1229 and 1047 (C=S); *v* (cm^{-1}) = 2231(CN). UV-Vis max (cyclohexane): 296 and 529 nm. GC-MS (EI): *m/e* = 221. Purity by HPLC = 99.4%.

2. Cumyl Dithiobenzoate (CumSS)

^{1}H NMR: δ (ppm): 2.00 (*s*, 6H, C***H*****$_3$**-C-C***H*****$_3$**), 7.85 (*d*, 2H, *o*-ArH of dithiobenzoate), 7.46 (*dd*, 1H, *p*-ArH of dithiobenzoate), 7.55 (*d*, 2H, *o*-ArH cumyl), 7.22 (*dd*, 1H, *p*-ArH cumyl), 7.31-7.39 (*m*, 4H, ArH cumyl). FT-IR: ν (cm^{-1}) = 1218 and 1042 (C=S). UV-Vis max (cyclohexane): 299 and 444 nm. GC-MS (EI): *m/e* = 272. Purity by HPLC = 99.8%.

3. Benzyl Dithiobenzoate (BzSS)

^{1}H NMR: δ (ppm): 4.6 (*s*, 2H, ***CH*****$_2$**-Ph), 8.00 (*d*, 2H, *o*-ArH of dithiobenzoate), 7.53 (*dd*, 1H, *p*-ArH of dithiobenzoate), 7.25-7.45 (*m*, 7H, ArH benzyl). FT-IR: ν (cm^{-1}) = 1226 and 1044 (C=S). UV-Vis max (cyclohexane): 302 and 504 nm. GC-MS (EI): *m/e* = 244. Purity by HPLC = 99.4%.

4. 1-Phenyl-2-benzoyloxy-ethyl Dithiobenzoate (BoESS)

^{1}H NMR: δ(ppm)：4.77-4.84 (*m*, 2H, CH-C***H*****$_2$**), 5.77-5.80 (*t*, 1H, C***H***-CH_2)，6.89-7.29 (*m*, ArH,11H)，7.91-8.08 (*d*, ArH,4H). UV-Vis max (cyclohexane): 298 and 514 nm. GC-MS：*m/e* = 378. Purity by HPLC = 99.4%.

5. 2-(Ethoxycarbonyl)prop-2-yl Dithiobenzoate (ECPSS)

^{1}H NMR: δ (ppm) = 1.24 (*t*, 3H, CH_2-C***H*****$_3$**), 1.76 (*s*, 6H, C***H*****$_3$**-C-C***H*****$_3$**), 4.16 (*q*, 2H, O-C***H*****$_2$**CH_3), 7.35 (*dd*, 2H, *m*-ArH), 7.52 (*dd*, 1H, *p*-ArH), 7.95 (*d*, 2H, *o*-ArH). FT-IR: *v* (cm^{-1}) = 1260 and 1042 (C=S); *v* (cm^{-1}) = 1732 (C=O). UV-Vis max (cyclohexane): 296 and 513 nm. GC-MS (EI): *m/e* = 268. Purity by HPLC = 99.8%.

The characterization results of Alkoxyamine

1. 1-(2′,2′,6′,6′-Tetramethylpiperidinyl-*N*-oxy)-1-phenylethane (PEON)

^{1}H NMR: δ (ppm) = 0.65 (*s*, CH_3, 3H), 1.02 (*s*, CH_3, 3H), 1.16 (*s*, CH_3, 3 H), 1.29 (*s*, CH_3, 3 H), 1.48 (*d*, CH-C***H*****$_3$**, 3 H), 1.3-1.6 (*m*, $(CH_2)_3$, 6H), 4.77 (*q*, C***H***-CH_3, 1 H), 7.21-7.33 (*m*, ArH, 5H). Purity by HPLC = 99.4%.

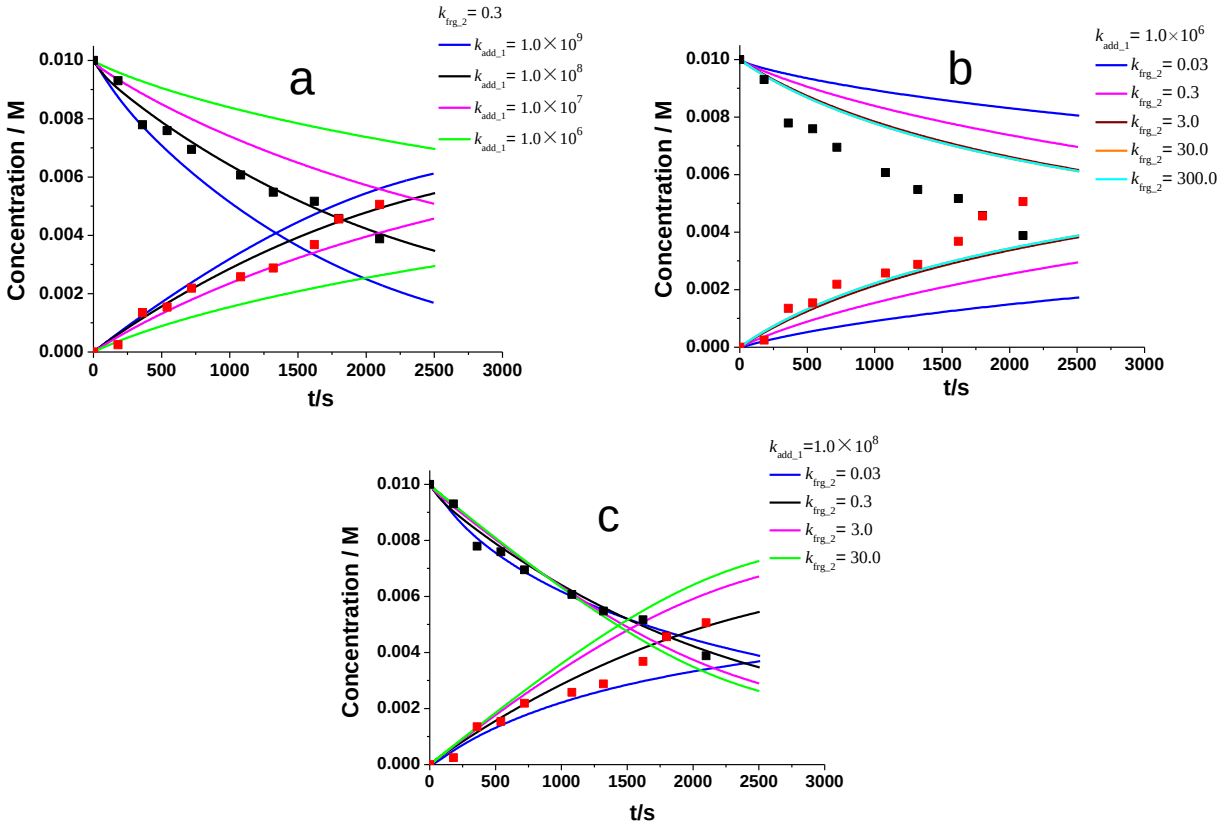

Figure S1. Sensitivity of the simulated kinetics on magnitudes of k_{add_1} (**a**) and k_{frg_2} (**b**, **c**), and kinetic fitting to the experimental results. Square: experimentally measured concentrations of starting dithioesters (black) and resulting dithioesters (red); Reaction conditions: **PEON** (0.261 g, 1.0 mmol) and **CNSS** (0.011g, 0.05 mmol) in *tert*-butyl benzene at 90 °C. Solid Lines: Monte Carlo simulation results with various values of k_{add_1} and k_{frg_2} (slow fragmentation model).

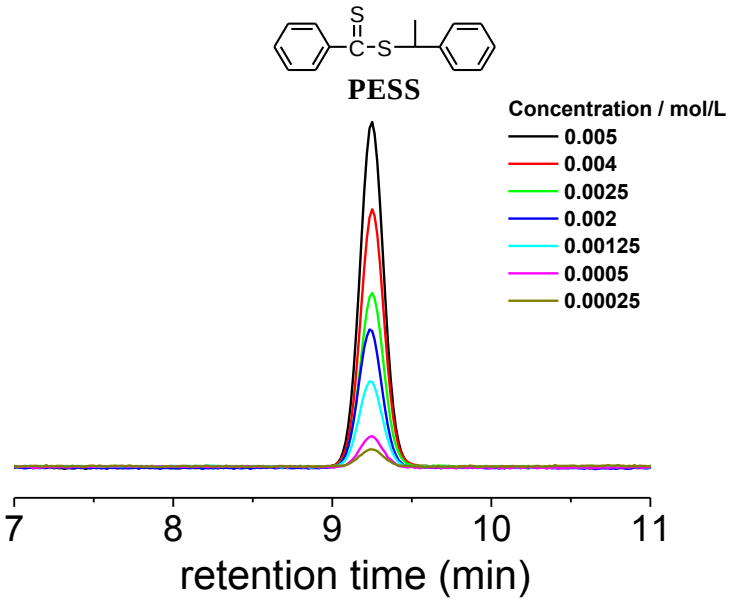

Figure S2. HPLC diagram of dithioester **PESS** in stock solutions of various concentrations for the purpose of calibration.

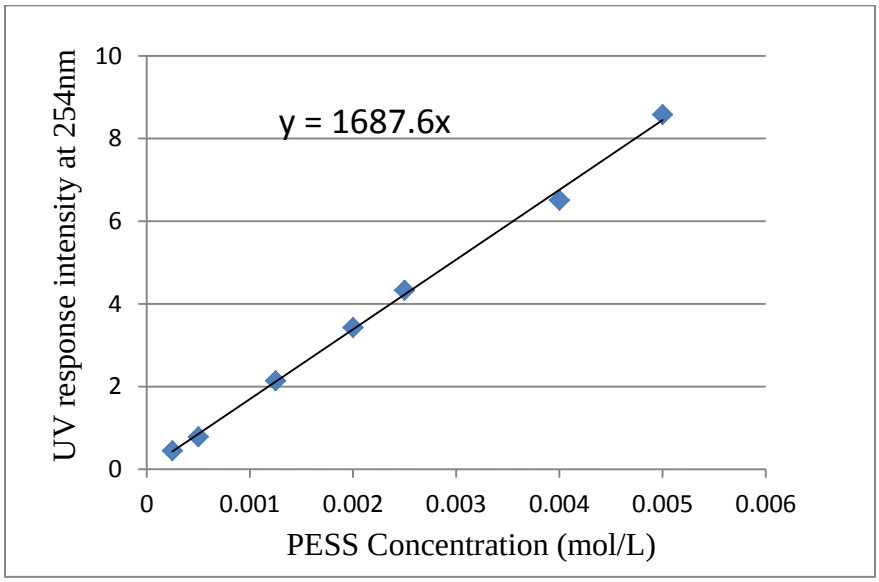

Figure S3. The calibration line for determining the concentration of PESS using UV detector at 254 nm.

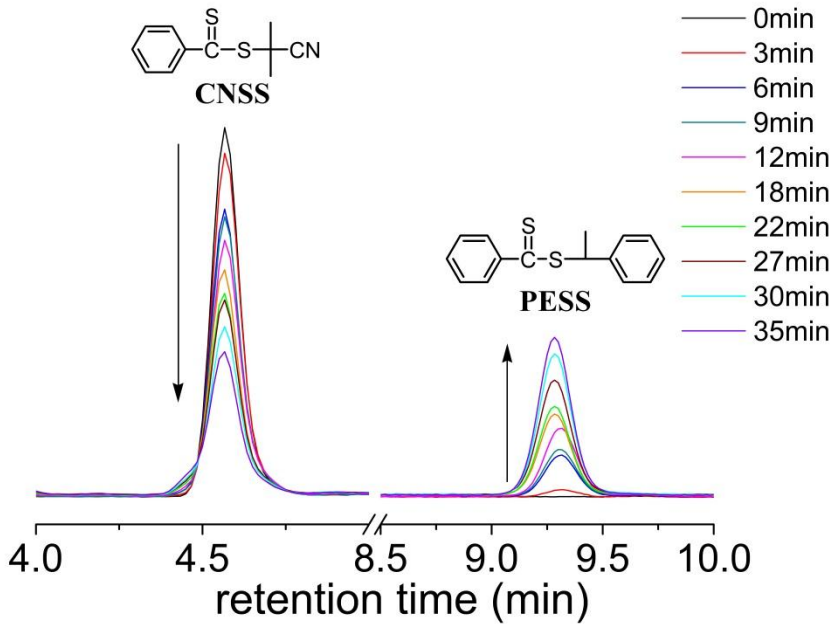

Figure S4. HPLC monitoring the concentration evolution of **CNSS** (starting dithioester) and **PESS** (resulting dithioester) versus the time for the cross reaction of **PEON** (0.261 g, 1.0 mmol) and **CNSS** (0.0110g, 0.05 mmol) in *tert*-butyl benzene at 90 °C.

Table S1. The experimental results of concentration of **CNSS** and **PESS** versus the time for the cross reaction of **PEON** and **CNSS**

Reaction time / min	**CNSS** Concentration / mol/L	**PESS** Concentration / mol/L
0	0.010	0
3	0.0093	0.00025
6	0.0078	0.0014
9	0.0076	0.0015
12	0.0070	0.0022
18	0.0061	0.0026
22	0.0055	0.0029
27	0.0052	0.0037
30	0.0046	0.0046
35	0.0039	0.0051

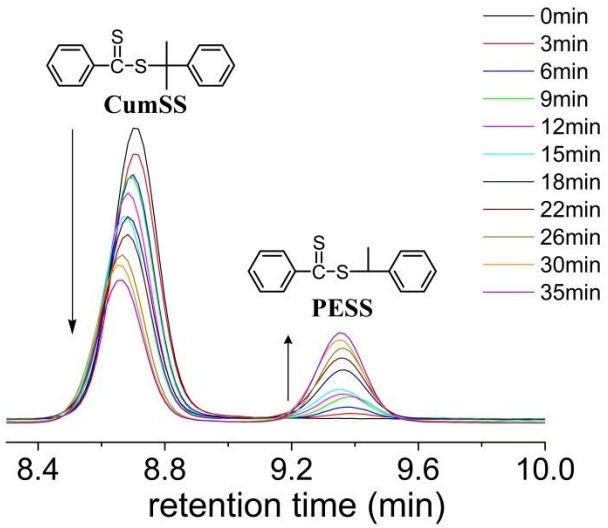

Figure S5. HPLC monitoring the concentration evolution of **CumSS** (starting dithioester) and **PESS** (resulting dithioester) versus the time for the cross reaction of **PEON** (0.261 g, 1.0 mmol) and **CumSS** (0.0136g, 0.05 mmol) in *tert*-butyl benzene at 90 °C.

Table S2. The experimental results of concentration of **CumSS** and **PESS** versus the time for the cross reaction of **PEON** and **CumSS**

Reaction time / min	CumSS Concentration / mol/L	PESS Concentration / mol/L
0	0.010	0
3	0.0091	0.00023
6	0.0084	0.00053
9	0.0084	0.0010
12	0.0078	0.0010
15	0.0070	0.0012
18	0.0069	0.0020
22	0.0064	0.0025
26	0.0058	0.0030
30	0.0054	0.0034
35	0.0049	0.0036

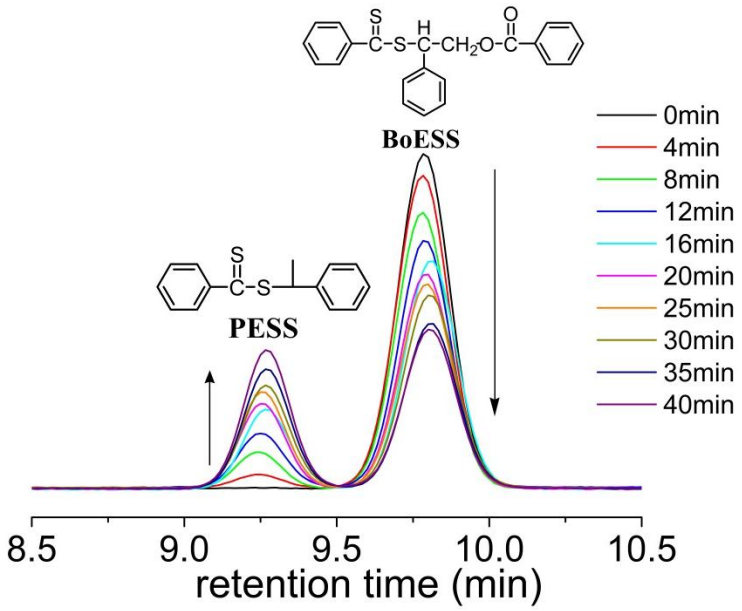

Figure S6. HPLC monitoring the concentration evolution of **BoESS** (starting dithioester) and **PESS** (resulting dithioester) versus the time for the cross reaction of **PEON** (0.261 g, 1.0 mmol) and **BoESS** (0.0189g, 0.05 mmol) in *tert*-butyl benzene at 90 °C.

Table S3. The experimental results of concentration of **BoESS** and **PESS** versus the time for the cross reaction of **PEON** and **BoESS**

Reaction time / min	BoESS Concentration / mol/L	PESS Concentration / mol/L
0	0.01	0
4	0.0094	0.00045
8	0.0083	0.0011
12	0.0074	0.0017
16	0.0068	0.0024
20	0.0064	0.0026
25	0.0061	0.0029
30	0.0058	0.0030
35	0.0049	0.0036
40	0.0048	0.0041

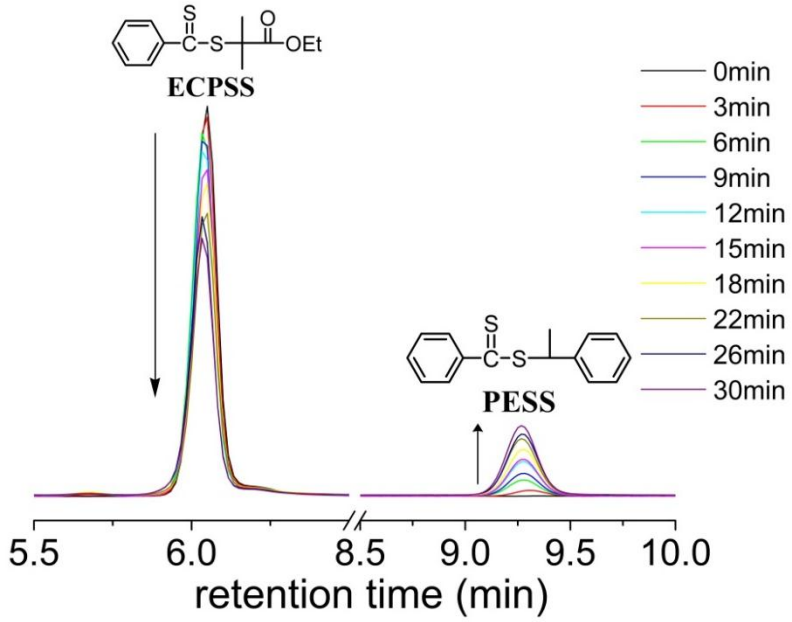

Figure S7. HPLC monitoring the concentration evolution of **ECPSS** (starting dithioester) and **PESS** (resulting dithioester) versus the time for the cross reaction of **PEON** (0.261 g, 1.0 mmol) and **ECPSS** (0.0134g, 0.05 mmol) in *tert*-butyl benzene at 90 °C.

Table S4. The experimental results of concentration of **ECPSS** and **PESS** versus the time for the cross reaction of **PEON** and **ECPSS**

Reaction time / min	ECPSS Concentration / mol/L	PESS Concentration / mol/L
0	0.01	0
3	0.0097	0.00020
6	0.0093	0.00050
9	0.0091	0.00073
12	0.0088	0.0011
15	0.0084	0.0012
18	0.0080	0.0015
22	0.0073	0.0018
26	0.0071	0.0020
30	0.0066	0.0022

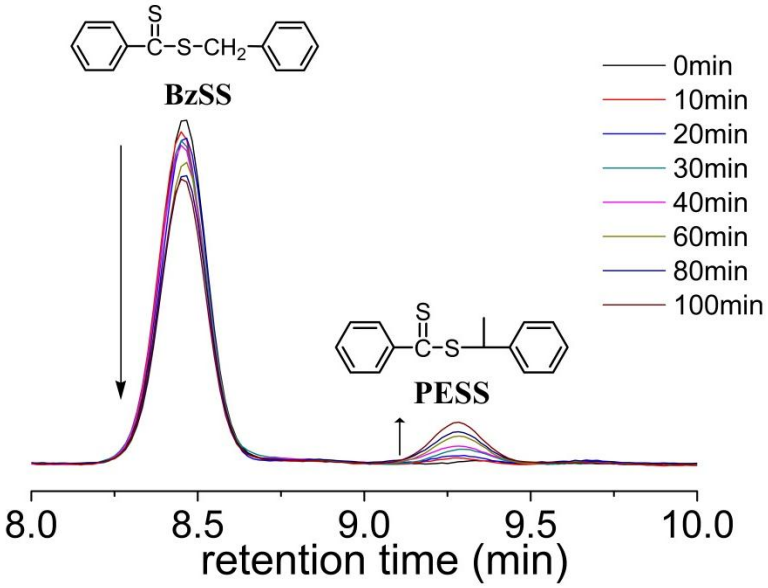

Figure S8. HPLC monitoring the concentration evolution of **BzSS** (starting dithioester) and **PESS** (resulting dithioester) versus the time for the cross reaction of **PEON** (0.261 g, 1.0 mmol) and **BzSS** (0.0122g, 0.05 mmol) in *tert*-butyl benzene at 90 °C.

Table S5. The experimental results of concentration of **BzSS** and **PESS** versus the time for the cross reaction of **PEON** and **BzSS**

Reaction time / min	BzSS Concentration / mol/L	PESS Concentration / mol/L
0	0.01	0
10	0.0097	0.00016
20	0.0095	0.00019
30	0.0094	0.00031
40	0.0092	0.00038
60	0.0088	0.00060
80	0.0084	0.00067
100	0.0083	0.00086