SUPPORTING INFORMATION

Cationic Ring Opening Polymerization Of Five Membered Cyclic Dithiocarbonate Having Tertiary Amine Moiety

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Contents

S2	¹ H and ¹³ C NMR of <i>N</i> , <i>N</i> -dibenzyl glycidylamine (DBGA)
S3	¹ H and ¹³ C NMR of 5-((dibenzylamino)methyl)-1,3-oxathiolane-2-thione (1)
S4	¹ H and ¹³ C NMR of 5-((diethylamino)methyl)-1,3-oxathiolane-2-thione (4)
S5	¹ H and ¹³ C NMR of Poly-1
S6	DEPT-135 of Poly-1
S7	¹ H and ¹³ C NMR of polymerization solution of 5-((diethylamino)methyl)-1,3-oxathiolane-2-
	thione (4)
S8	DEPT-135 of polymerization solution of 5-((diethylamino)methyl)-1,3-oxathiolane-2-thione
	(4)
S9	¹ H and ¹³ C NMR of stoichiometric reaction of 1 and MeOTf
S10	¹ H and ¹³ C NMR <i>N</i> , <i>N</i> , <i>N</i> -tribenzyl- <i>N</i> -methyl ammonium triflate
S11	¹ H and ¹³ C NMR N, N, N-triethyl-N-methyl ammonium triflate
S12	Mass Spectra of 5-((dibenzylamino)methyl)-1,3-oxathiolane-2-thione (1) and 5-
	((diethylamino)methyl)-1,3-oxathiolane-2-thione (4)
S13	IR spectra of 5-((dibenzylamino)methyl)-1,3-oxathiolane-2-thione (1) and Poly-1
S14	IR spectra of 5-((diethylamino)methyl)-1,3-oxathiolane-2-thione (4)
S15	TGA and DSC profile of Poly-1
S16	Table 1 of XRC analysis
S17	Time-Conversion study of Cationic Polymerization of 5-((dibenzylamino)methyl)-1,3-
	oxathiolane-2-thione (1) to Poly-1 at room temperature
S18	SEC profiles before and after the post-polymerization experiment of 5-
	((dibenzylamino)methyl)-1,3-oxathiolane-2-thione (1) to Poly-1

Fig-S1. ¹H NMR of *N*, *N*-dibenzyl glycidylamine (DBGA)



Fig-S2. ¹³C NMR *N*, *N*-dibenzyl glycidylamine (DBGA)





Fig-S4. ¹³C NMR of 5-((dibenzylamino)methyl)-1,3-oxathiolane-2-thione (1)







Fig-S6. ¹³C NMR of 5-((diethylamino)methyl)-1,3-oxathiolane-2-thione (4)



Fig-S7. ¹H NMR of Poly-1



Fig-S9. DEPT135 of Poly-1



Fig-S10. ¹H NMR of polymerization solution of 4



Fig-S12. DEPT-135 of polymerization solution of 4



Fig-S13. ¹H NMR of stoichiometric reaction of 5-((dibenzylamino)methyl)-1,3-oxathiolane-2-thione (1) with MeOTf



Fig-S14. ¹³C NMR of stoichiometric reaction of 5-((dibenzylamino)methyl)-1,3-oxathiolane-2-thione (1) with MeOTf







Fig-S16 ¹³C NMR of *N*, *N*, *N*-tribenzyl-*N*-methyl ammonium triflate



Fig-S17 ¹H NMR of *N*, *N*, *N*-triethyl-*N*-methyl ammonium triflate



Fig-S18 ¹³C NMR of *N*, *N*, *N*-triethyl-*N*-methyl ammonium triflate





Fig-S19. Positive FAB Mass Spectra of 5-((dibenzylamino)methyl)-1,3-oxathiolane-2-thione (1) ([M+H]⁺ = 330)

Fig-S20. Positive FAB Mass Spectra of **5-((diethylamino)methyl)-1,3-oxathiolane-2-thione (4)** ([M+H]+ = 206)





Fig-S21. IR Spectra of 5-((dibenzylamino)methyl)-1,3-oxathiolane-2-thione (1)

Fig-S22. IR Spectra of Poly-1



Fig-S23. IR Spectra of 5-((diethylamino)methyl)-1,3-oxathiolane-2-thione (4)











5-((dibenzylamino)methyl)-1,3-oxathiolane-2-thione
(1)
$C_{18}H_{19}N_1O_1S_2$
329.46
90
orthorhombic
$P2_12_12_1$
8.4425(4)
10.2492(3)
19.6013(8)
90
90
90
1696.08(12)
4
1.290
2.841
696.0
$0.055 \times 0.047 \times 0.029$
9.024 to 152.446°
$-9 \le h \le 10, -12 \le k \le 8, -20 \le 1 \le 24$
9646
3384[R(int) = 0.0222]
3384/0/199
1.072
$R_1 = 0.0243, wR_2 = 0.0624$
$R_1 = 0.0257, wR_2 = 0.0630$
0.18/-0.18
0.056(6)

Table 1. Crystal data and structure refinement for 5-((dibenzylamino)methyl)-1,3-oxathiolane-2-thione (1)



Time-Conversion study of Cationic Polymerization of 5-((dibenzylamino)methyl)-1,3-oxathiolane-2-thione (1) to Poly-1 at room temperature

To a solution of 1 (0.329 g, 1.0 mmol) in chlorobenzene (1.0 mL) was added MeOTf (5 mol%, 5 μ L; [M]₀/[I]₀= 20) and stirred at ambient temperature. To measure the conversion at 30 min, 1h, 2h, 3h, 4h and 6h an aliquot was taken quenched with TEA, then ¹H NMR and GPC of the sample was measured to determine the conversion and molar mass (M_n) respectively.



Figure S26: Time-conversion plot for the polymerization of 5-((dibenzylamino)methyl)-1,3-oxathiolane-2-thione (1) with MeOTf in chlorobenzene (1.0 M) at 30 °C, ($[1]_0/[MeOTf]_0 = 20.0$)



Figure S27. SEC profiles before and after the post-polymerization experiment of 1 to Poly-1: first-stage polymerization, $M_n = 11061$, $M_w/M_n = 1.32$; Poly-1: post polymer obtained in the second stage polymerization, $M_n = 11568$, $M_w/M_n = 1.40$