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Supporting Information

Magnesium Complexes Containing Biphenyl-based Tridentate Iminophenolate Ligands for Ring-Opening Polymerization of *rac*-Lactide and α-Methyltrimethylene Carbonate

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Table S1. The chemical shifts of dimethyl amino resonances in the ^{1}H NMR spectra of magnesium complexes and corresponding proligands [a]

Complex	Ar-N(CH_3)$_2$		Ligand	Ar-N(CH_3)$_2$
	C_6D_6	C_6D_6 with THF[b]		C_6D_6
1	--	2.22 (s) [c]	**L^{1}H**	2.37
2	2.22 (br)	2.10 (s)	**L^{2}H**	2.21
3	--	2.23 (s)[c]	**L^{3}H**	2.17
4	2.55 (br)	2.10 (s)	**L^{4}H**	2.32

[a]: In ppm; [b]: One tiny drop of THF was added to the solution of magnesium complex in C_6D_6; [c]: The corresponding resonance of complexes **1** and **3** in C_6D_6.

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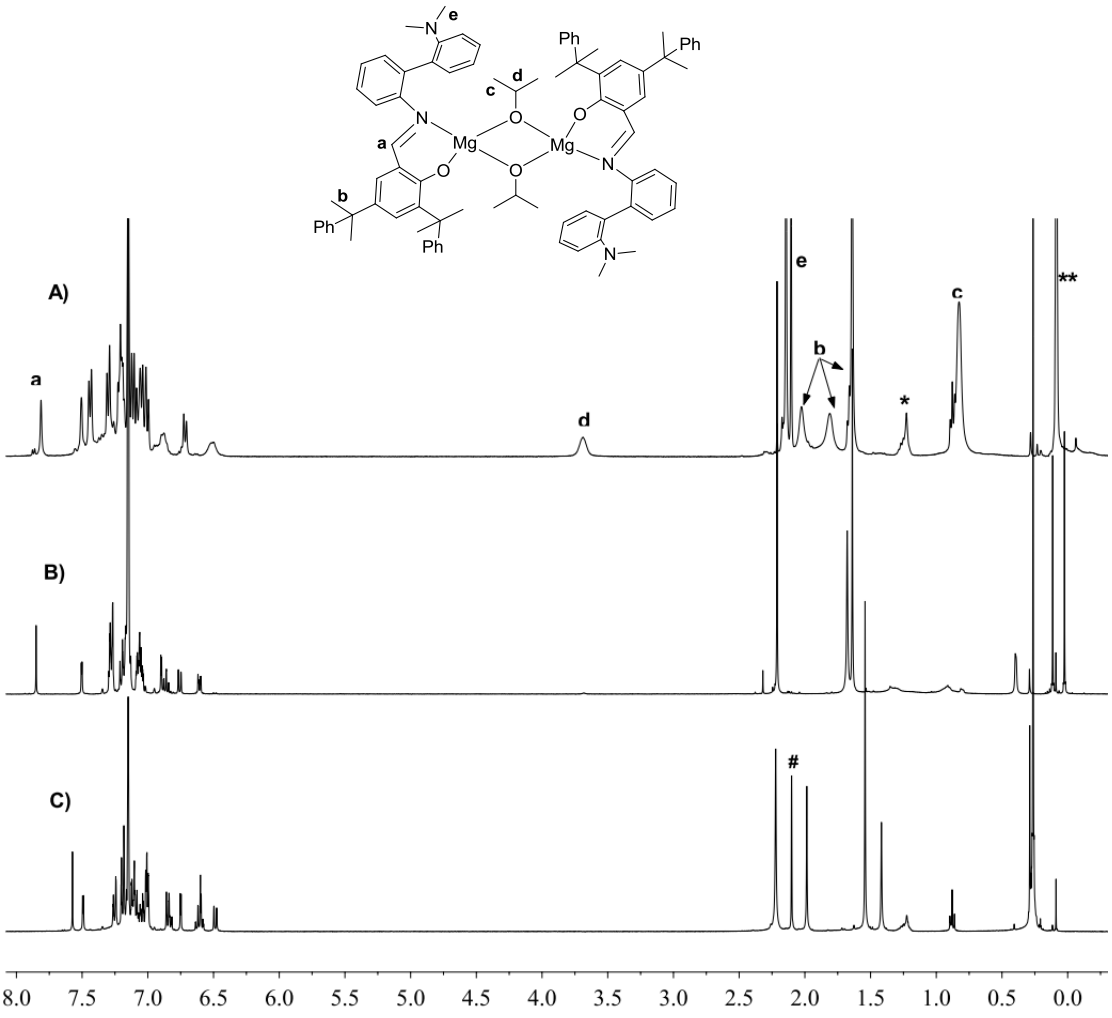

Figure S1. A) ^{1}H NMR trace spectrum of reaction between complex **2** and one equiv. of 2-propanol; B) ^{1}H NMR spectrum of free ligand $\mathbf{L^{2}H}$; C) ^{1}H NMR spectrum of complex **2** (C_6D_6, 400 MHz, *, hexane; **, $HN(SiMe_3)_2$; #, methyl signal of toluene)

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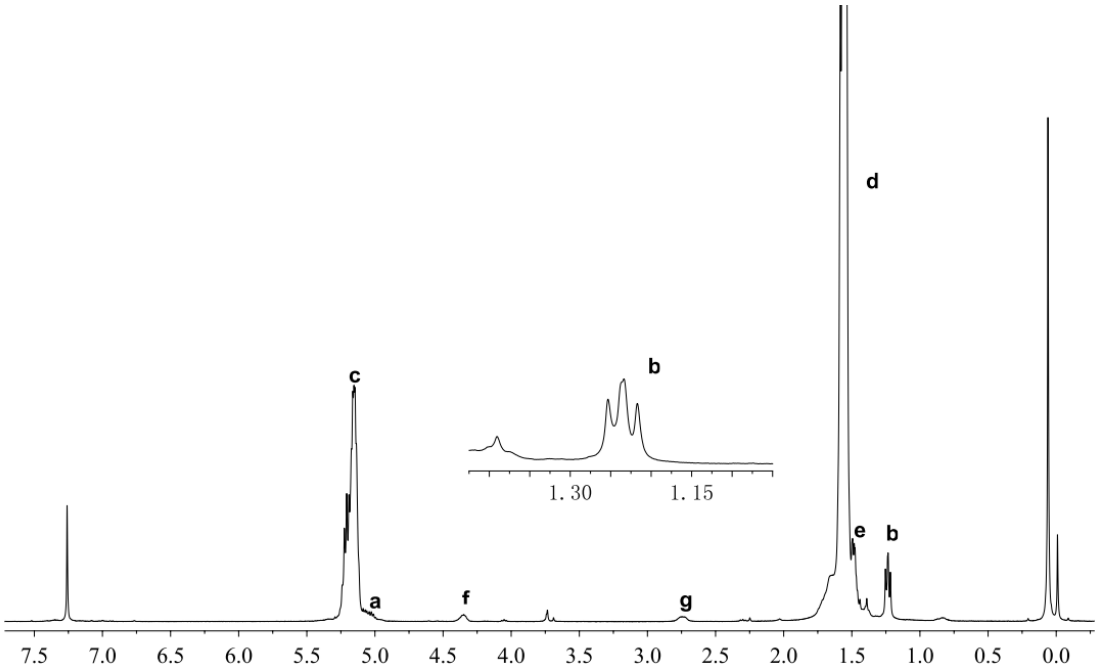

Figure S2. ^{1}H NMR spectrum of *rac*-lactide oligomer obtained by complex **2**/^{i}PrOH system ([*rac*-LA]$_0$: [Mg]$_0$: [^{i}PrOH]$_0$ = 20:1:1, at 25 ºC) in $CDCl_3$.

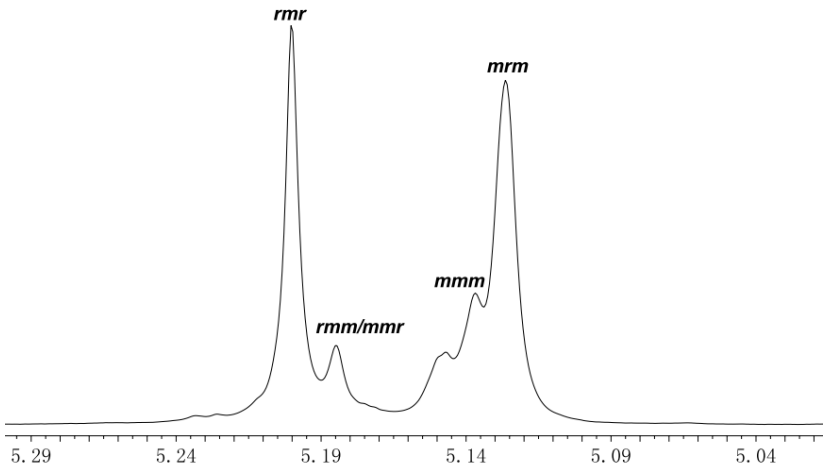

Figure S3. Homonuclear decoupled ^{1}H NMR spectrum of PLA produced from *rac*-lactide using **3** as initiator. ([*rac*-LA]$_0$ = 1 M, [**3**] = [^{i}PrOH] = 0.5 mM, 94% monomer conv., in THF, 25 ^{o}C, P_r = 0.77.)

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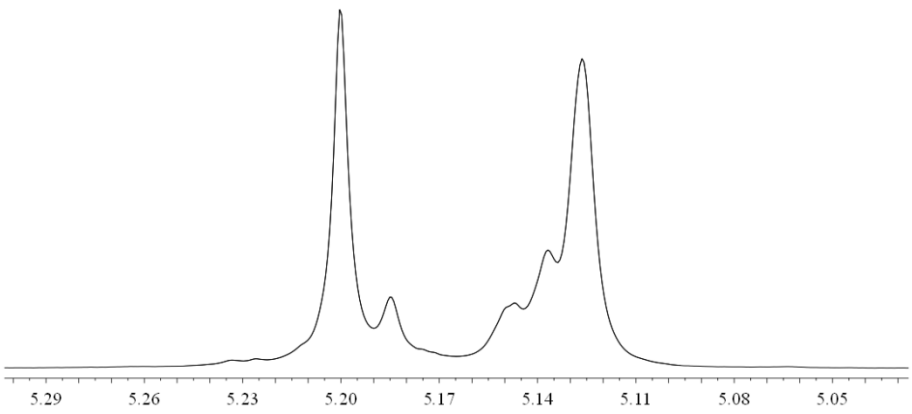

Figure S4. Homonuclear decoupled ^{1}H NMR spectrum of PLA produced from *rac*-lactide using **3** as initiator. ([*rac*-LA]$_0$ = 1 M, [**3**] = [^{i}PrOH] = 0.5 mM, 73% monomer conv., in THF, –38 ^{o}C, P_r = 0.81.)

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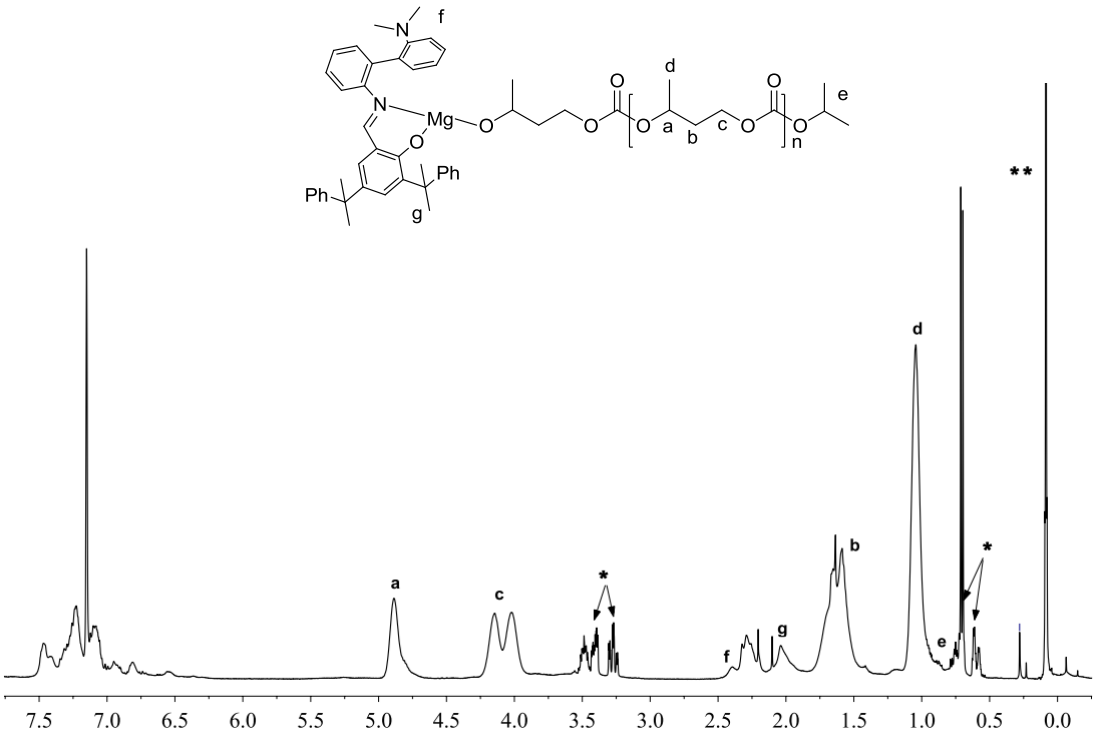

Figure S5. ^{1}H NMR spectrum of active α-MeTMC oligomer by **2**/^{i}PrOH ([α-MeTMC]$_0$: [Mg]$_0$: [^{i}PrOH]$_0$ = 20:1:1; 20 ºC, C_6D_6, 400 MHz; *, monomer; **, free $HN(SiMe_3)_2$).

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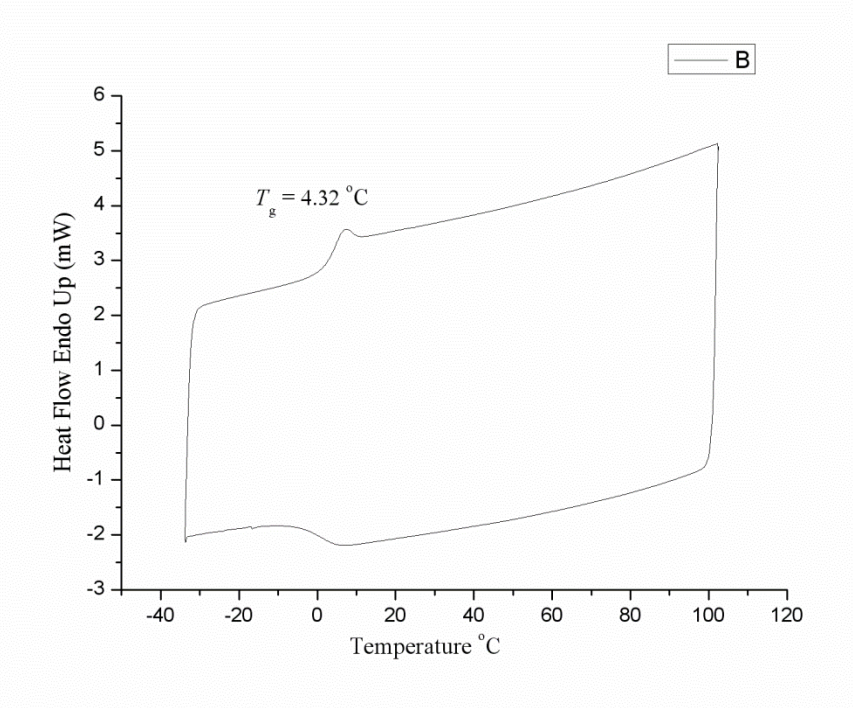

Figure S6. The DSC curves of poly(α-MeTMC) produced from α-MeTMC using **1** as initiator. ($[\alpha\text{-MeTMC}]_0$ = 1 M, [**1**] = 0.5 mM, 90% monomer conv., in toluene, 70 °C, T_g= 4.32 °C.)

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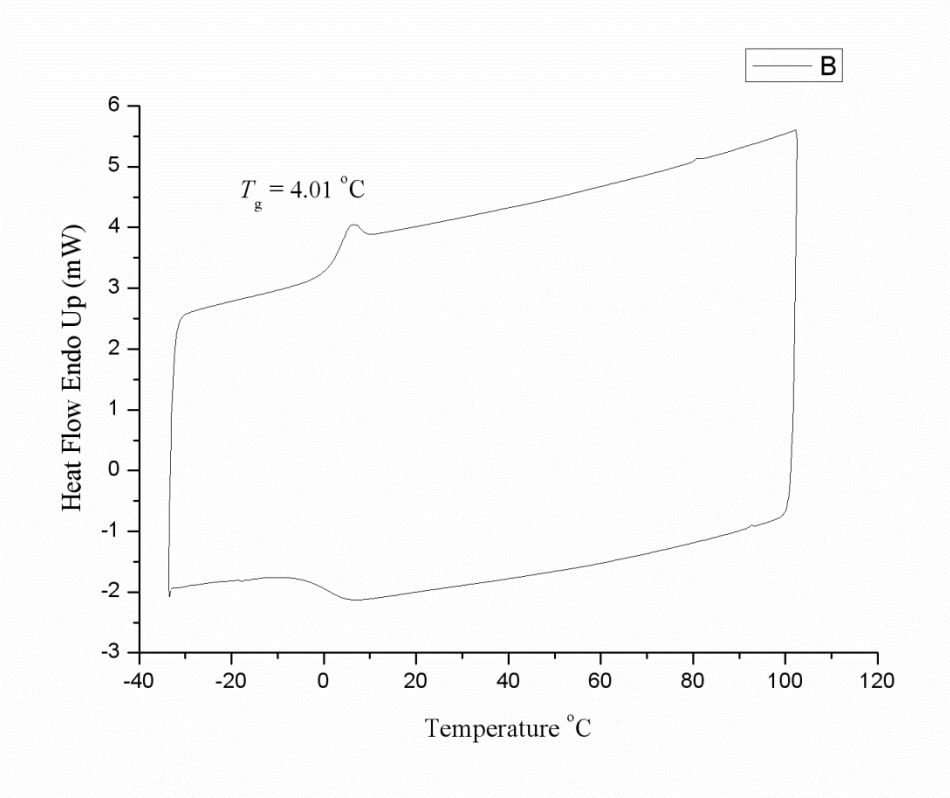

Figure S7. The DSC curves of poly(α-MeTMC) produced from α-MeTMC using **2** as initiator. ($[\alpha\text{-MeTMC}]_0$ = 1 M, [**2**] = 0.5 mM, 90% monomer conv., in toluene, 70 °C, T_g = 4.01 °C.)

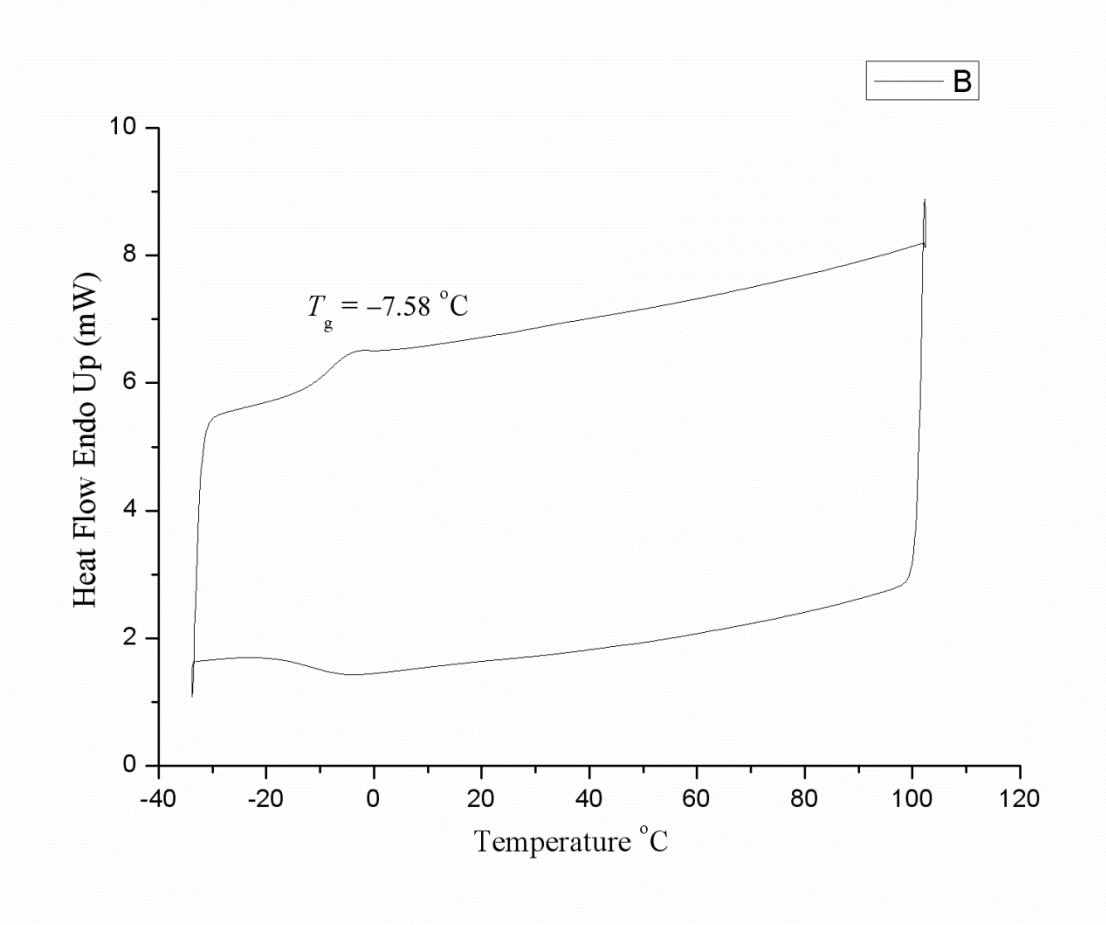

Figure S8. The DSC curves of poly(α-MeTMC) produced from α-MeTMC using **3** as initiator. ($[\alpha\text{-MeTMC}]_0$ = 1 M, [**3**] = 0.5 mM, 92% monomer conv., in toluene, 70 °C, T_g = –7.58 °C.)

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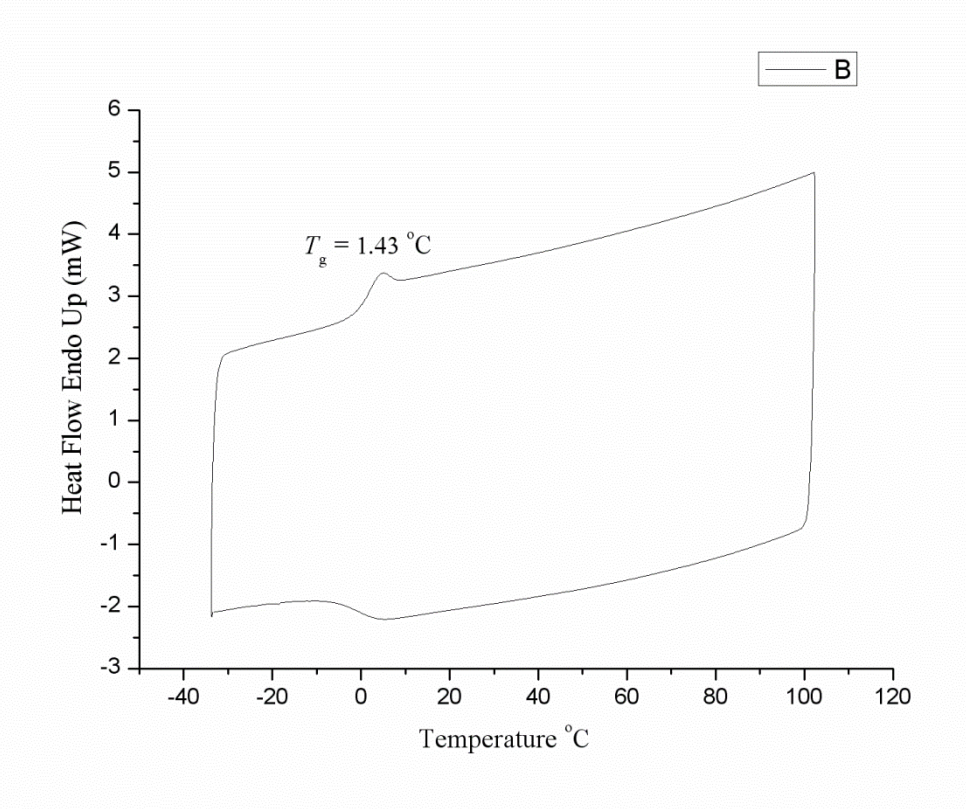

Figure S9. The DSC curves of poly(α-MeTMC) produced from α-MeTMC using **4** as initiator. ($[\alpha\text{-MeTMC}]_0$ = 1 M, [**4**] = 0.5 mM, 88% monomer conv., in toluene, 70 °C, T_g = 1.43 °C.)