

Supporting Information to

Manganese(III) Acetylacetonate Initiated RAFT Polymerizations:

An Alternative and Versatile RAFT Initiator

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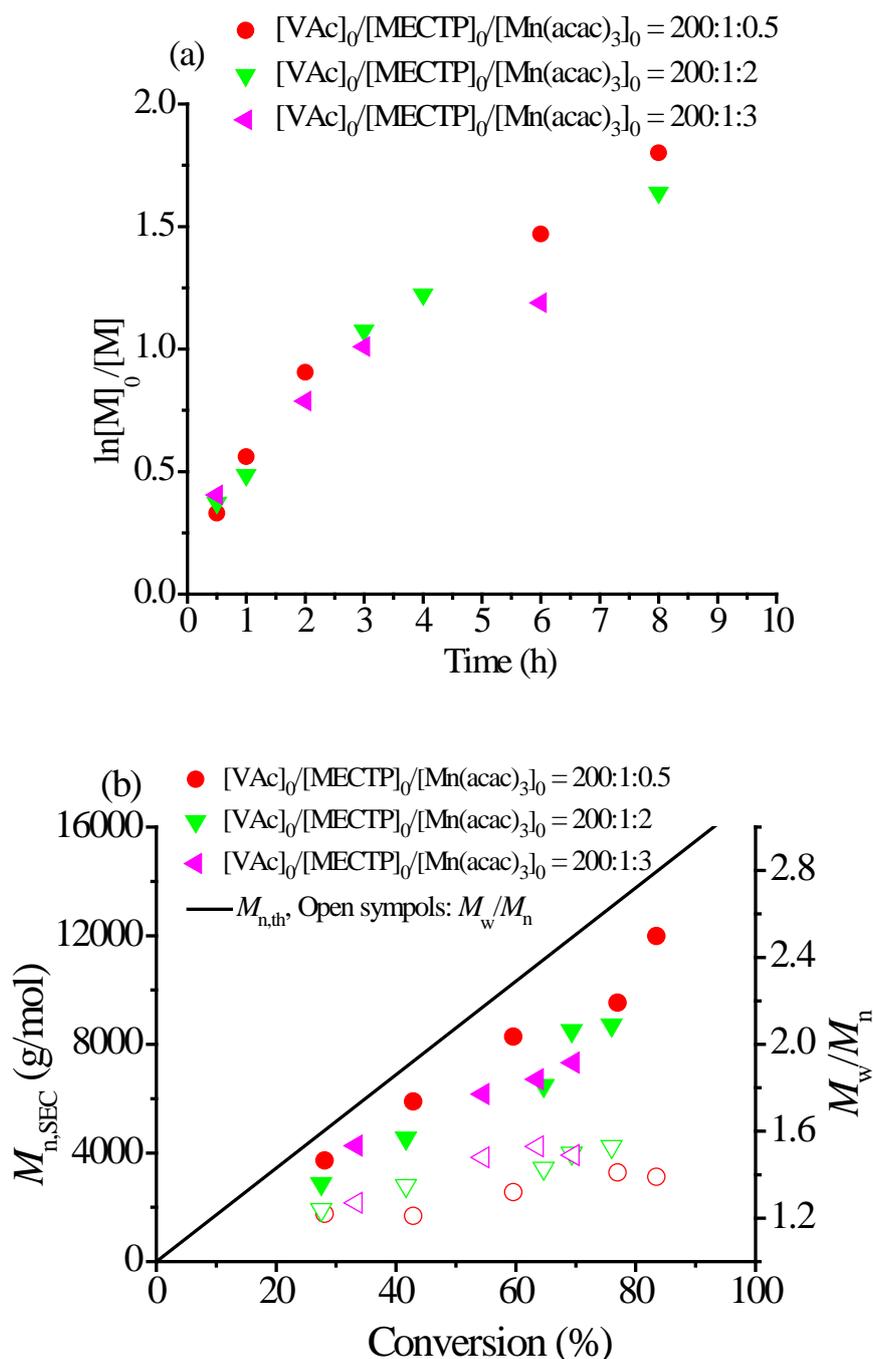


Figure S1. (a) Kinetic investigation ($\ln([M]_0/[M])$ versus time) and (b) Dependence of $M_{n,SEC}$ and M_w/M_n on the conversion of the bulk polymerization of VAc mediated by $Mn(acac)_3$ in combination with MECTP at 80 °C with different amount of $Mn(acac)_3$. VAc = 1.0 mL. $[M]_0$ and $[M]$ refer to the initial concentration and instant concentration of VAc, respectively. $M_{n,th} = ([VAc]_0/[MECTP]_0) \times M_{VAc} \times \text{Conversion} + M_{MECTP}$, where M_{VAc} and M_{MECTP} represent the molecular weights of VAc and MECTP, respectively.

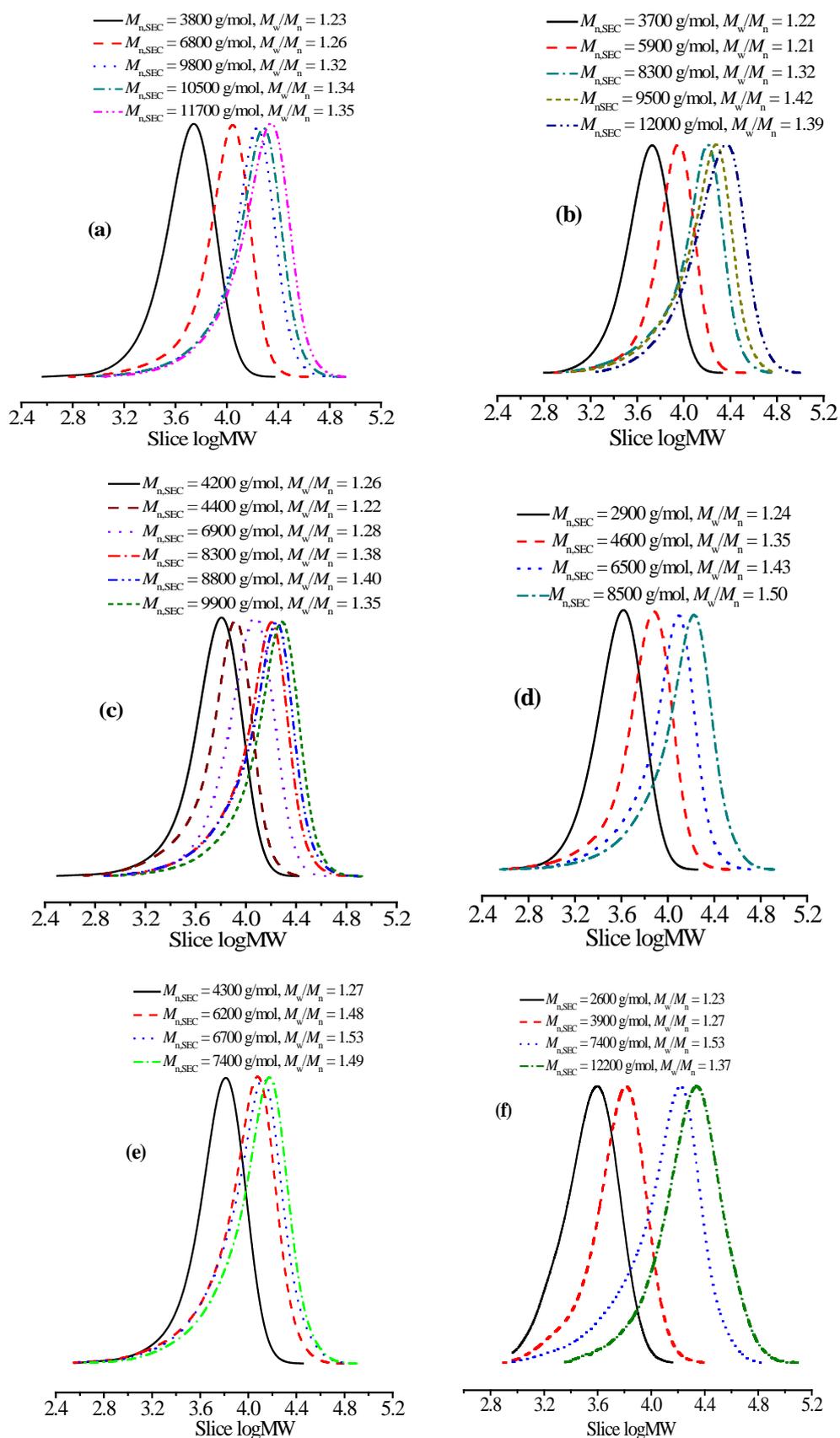


Figure S2. Evolution of SEC traces: (a) $[VAc]_0/[MECTP]_0/[Mn(acac)_3]_0 = 200:1:0.2$; (b) $[VAc]_0/[MECTP]_0/[Mn(acac)_3]_0 = 200:1:0.5$; (c) $[VAc]_0/[MECTP]_0/[Mn(acac)_3]_0 = 200:1:1$; (d) $[VAc]_0/[MECTP]_0/[Mn(acac)_3]_0 = 200:1:2$; (e) $[VAc]_0/[MECTP]_0/[Mn(acac)_3]_0 = 200:1:3$; (f) $[VAc]_0/[MECTP]_0/[Mn(acac)_3]_0 = 200:1:4$.

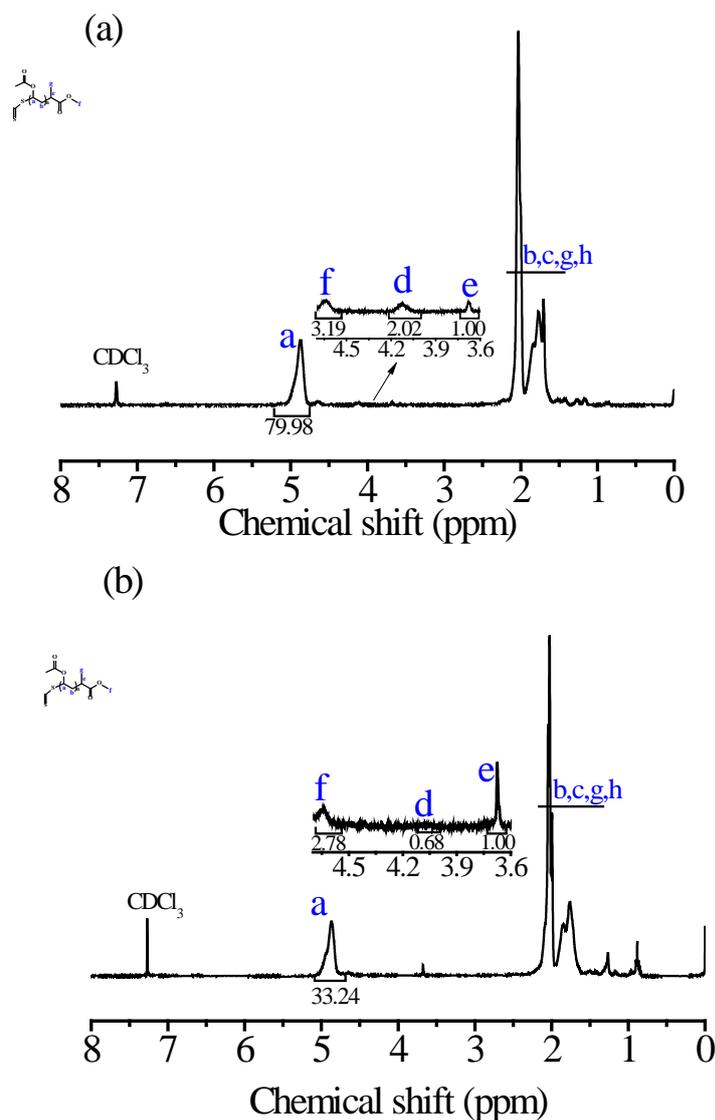


Figure S3. ^1H NMR spectrum of PVAc obtained in the presence of MECTP with (a) $\text{Mn}(\text{acac})_3$ ($M_{n,\text{SEC}} = 6800$ g/mol, $M_w/M_n = 1.26$) and (b) AIBN ($M_{n,\text{SEC}} = 6900$ g/mol, $M_w/M_n = 1.33$), respectively. CDCl_3 was used as the solvent and tetramethylsilane (TMS) as the internal standard. Polymerization conditions: $[\text{VAc}]_0/[\text{MECTP}]_0/[\text{Mn}(\text{acac})_3]_0$ (or $[\text{AIBN}]_0$) = 200/1/0.2, $\text{VAc} = 1.0$ mL temperature = 80°C .

The chain end of the PVAc sample prepared in the presence of $\text{Mn}(\text{acac})_3$ and MECTP was analyzed by ^1H NMR spectroscopy (**Figure S3a**). The PVAc sample ($M_{n,\text{SEC}} = 6800$ g/mol, $M_w/M_n = 1.26$) was obtained at 48.4% conversion from the polymerization with $[\text{VAc}]_0/[\text{MECTP}]_0/[\text{Mn}(\text{acac})_3]_0 = 200:1:0.2$ (**Figure 1**). The signals at $\delta = 4.10$ ppm (2H, integral value = $I_{4.10} = 2.02$) could be assigned to the protons of the methylene from xanthate (MECTP), which revealed that the moieties of MECTP were attached to the polymer chain ends (ω chain end). The signals at $\delta = 4.60$ - 5.40 ppm in the ^1H NMR spectrum were assigned

to the protons of methine in PVAc repeat units (H, integral value = $I_{4.90} = 79.98$). Assuming that each polymer chain was captured by a MECTP moiety, the molecular weight ($M_{n,NMR}$) of PVAc can be calculated from the integrals in ^1H NMR, according to eq 1:

$$M_{n,NMR} \text{ (g/mol)} = (I_{4.90}/1) \times 86.09/(I_{4.10}/2) + 208.02 \quad (\text{S1})$$

where 86.09 and 208.02 are the molecular weights of VAc and MECTP, respectively. The molecular weight of PVAc sample calculated from the ^1H NMR spectrum ($M_{n,NMR}$) was 7000 g/mol, which was close to the SEC value (6800 g/mol), indicating that the PVAc was end-capped by MECTP species with high chain end fidelity ($F_n = 97.1\%$). While the PVAc obtained with AIBN replaced of $\text{Mn}(\text{acac})_3$ got a poorer fidelity ($F_n = 80.2\%$, **Figure S3b**).

The living nature of the polymer was further confirmed by chain extension reaction upon the addition of fresh VAc monomer. The PVAc sample ($M_{n,SEC} = 9400$ g/mol, $M_w/M_n = 1.25$) obtained by RAFT polymerization with $\text{Mn}(\text{acac})_3$ in combination with MECTP was used as the macroinitiator. The chain extension was successful at 80 °C in the presence of $\text{Mn}(\text{acac})_3$. Much higher molecular weight of PVAc ($M_{n,SEC} = 19400$ g/mol) was obtained as shown in Figure S4. It is clear from this result that most of the end groups are active for participation in chain extension reaction, and the xanthate end group can be reactivated as the macroinitiator.

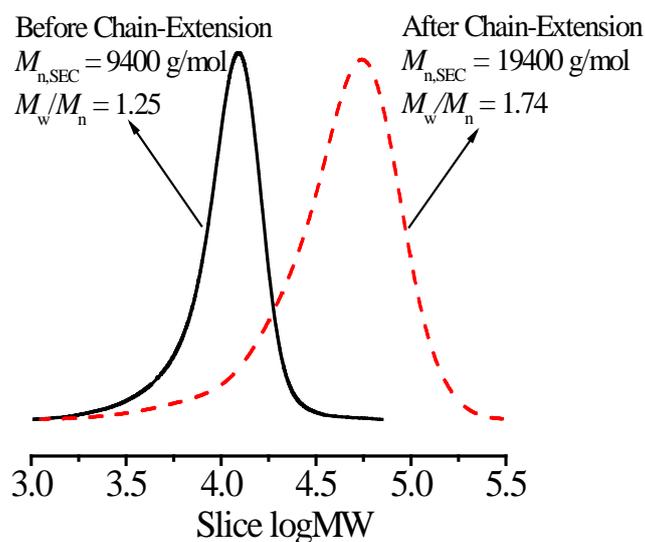


Figure S4. SEC curves before and after chain extension with PVAc as the macro-initiator at 80 °C. $[\text{VAc}]_0/[\text{PVAc}]_0/[\text{Mn}(\text{acac})_3]_0 = 500/1/1$, VAc = 1.0 mL, 5 hrs, 40.1% conversion.

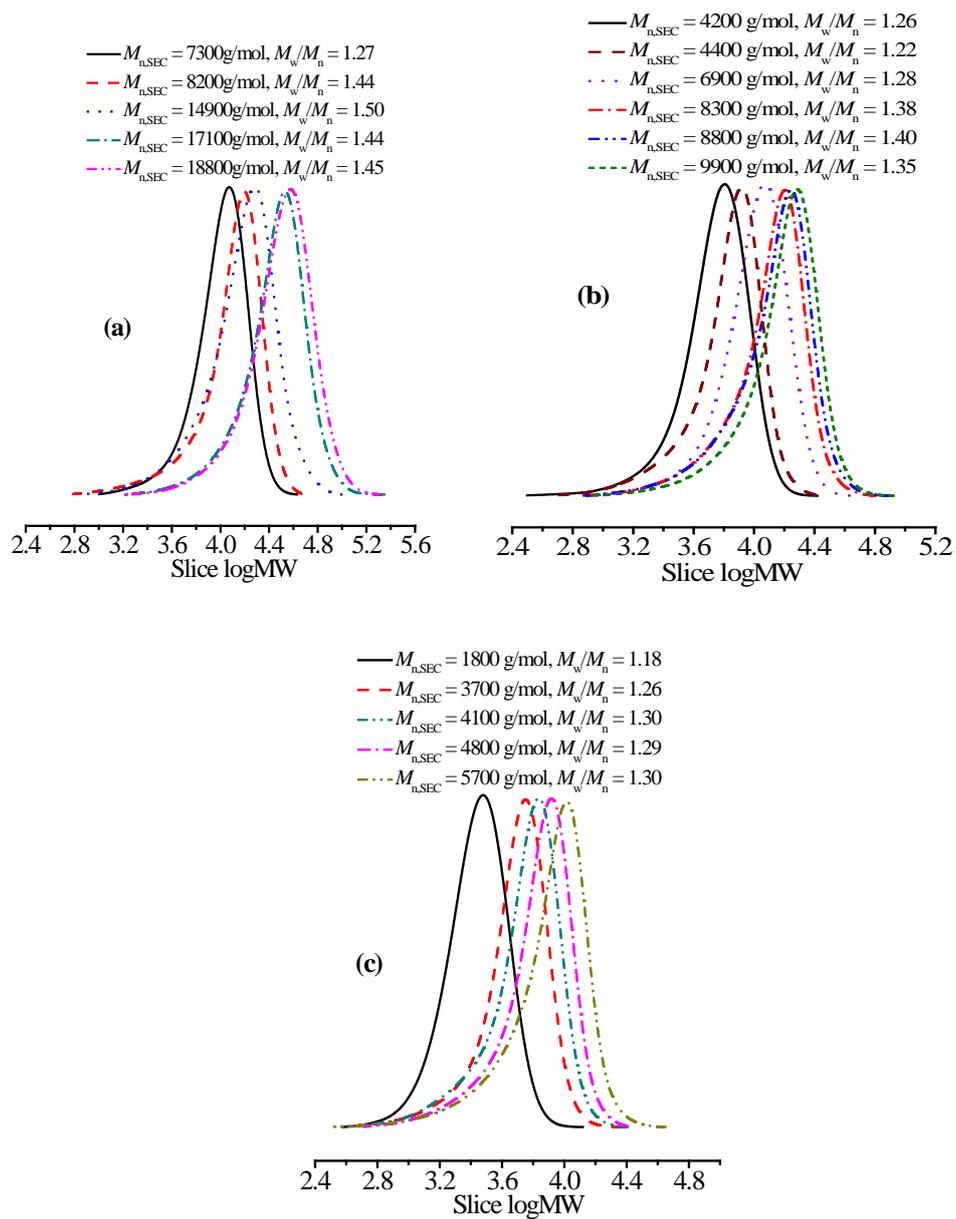


Figure S5. Evolution of SEC traces: (a) [VAc]₀/[MECTP]₀/[Mn(acac)₃]₀ = 200:0.5:1; (b) [VAc]₀/[MECTP]₀/[Mn(acac)₃]₀ = 200:1:1; (c) [VAc]₀/[MECTP]₀/[Mn(acac)₃]₀ = 200:2:1.

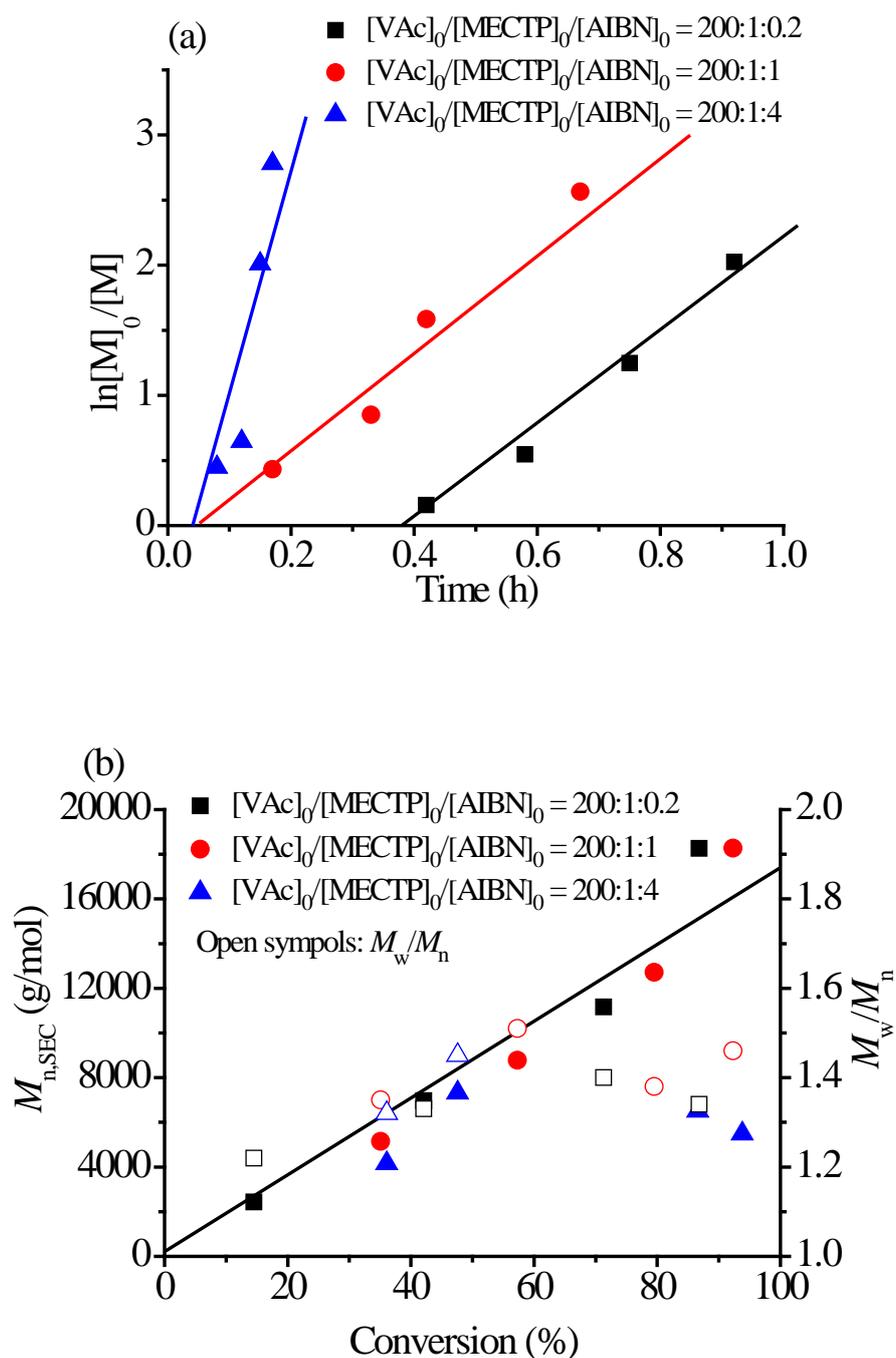


Figure S6. (a) Kinetic investigation ($\ln([M]_0/[M])$ versus time) and (b) Dependence of $M_{n,SEC}$ and M_w/M_n on the conversion of the bulk polymerization of VAc mediated by AIBN in combination with MECTP at 80 °C with different amount of AIBN. VAc = 1.0 mL. $[M]_0$ and $[M]$ refer to the initial concentration and instant concentration of VAc, respectively. $M_{n,th} = ([VAc]_0/[MECTP]_0) \times M_{VAc} \times \text{Conversion} + M_{MECTP}$, where M_{VAc} and M_{MECTP} represent the molecular weights of VAc and MECTP, respectively.

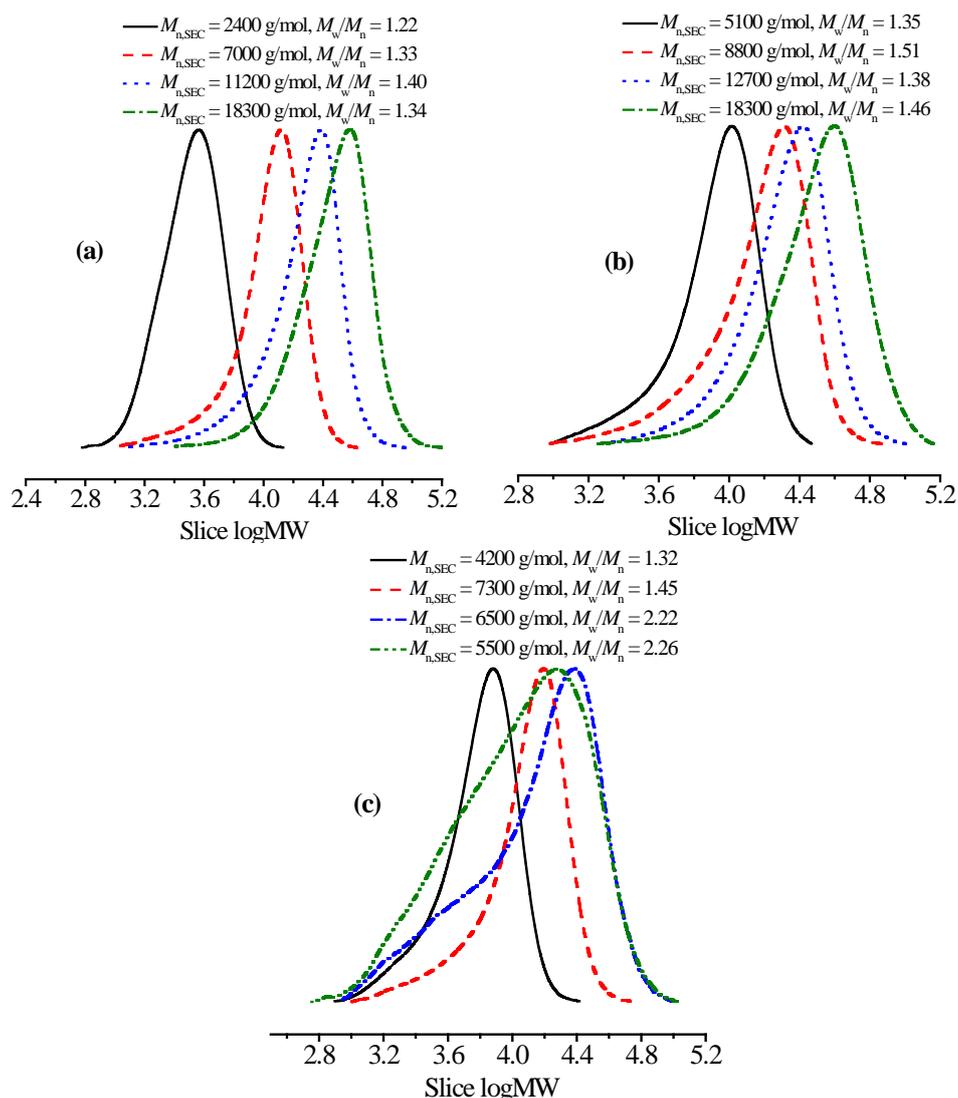


Figure S7. Evolution of SEC traces: (a) $[VAc]_0/[MECTP]_0/[AIBN]_0 = 200:1:0.2$; (b) $[VAc]_0/[MECTP]_0/[AIBN]_0 = 200:1:1$; (c) $[VAc]_0/[MECTP]_0/[AIBN]_0 = 200:1:4$.

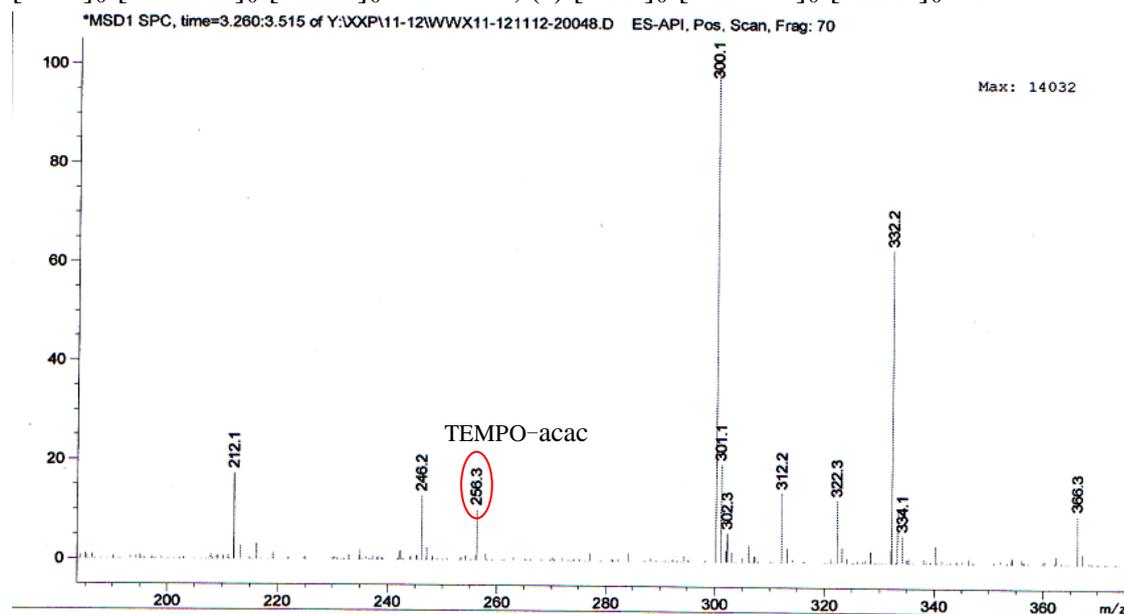


Figure S8. LC-MS spectrum of $[TEMPO]_0/[MECTP]_0/[Mn(acac)_3]_0 = 1/1/1$ in MeCN, after reacted for 1 day at 80 °C under the protection of Ar.

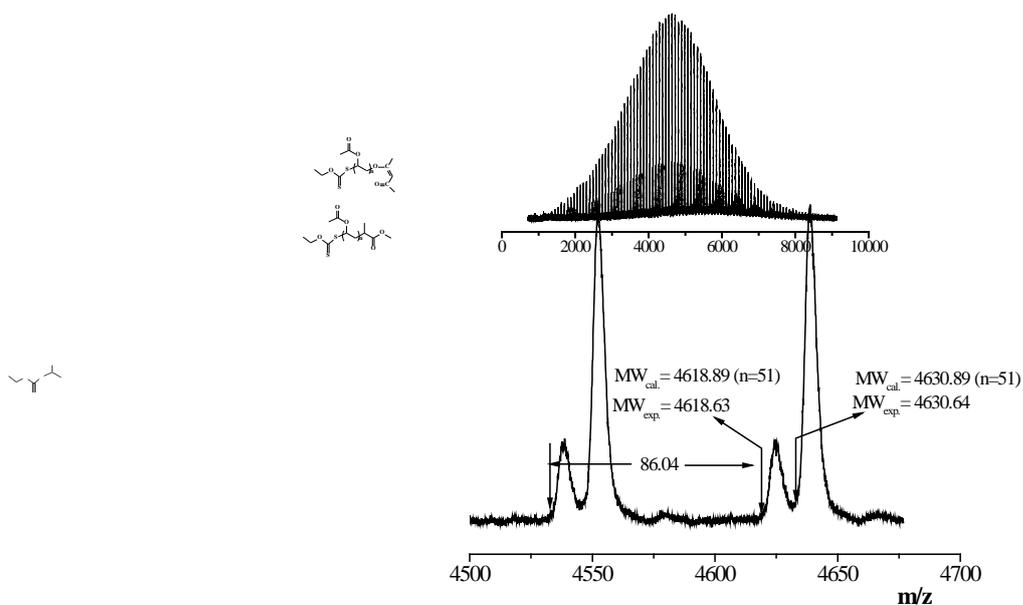


Figure S9. Matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry of poly(vinyl acetate) (PVAc, $M_{n,SEC} = 5500$, $M_w/M_n = 1.23$) from $Mn(acac)_3$ initiated RAFT polymerization of VAc.

Figure S10 showed the 1H NMR spectroscopy of the PMMA sample prepared in the presence of CPDN and $Mn(acac)_3$. The signals at $\delta = 7.35$ -8.15 ppm (7H, integral value = $I_{8.1} = 0.36$) were corresponded to the aromatic protons of the naphthalene units in CPDN,¹ which revealed that the dithiocarbonate moieties of CPDN were attached to the polymer chain ends (ω chain end). The signals at $\delta = 3.30$ -3.90 ppm in the 1H NMR spectrum were assigned to the protons of methoxy in PMMA repeat units (3H, integral value = $I_{3.60} = 12.46$). Assuming that each polymer chain was captured by a naphthyl moiety from CPDN, the molecular weight ($M_{n,NMR}$) of PMMA can be calculated from the integrals in 1H NMR, according to eq S2:

$$M_{n,NMR} \text{ (g/mol)} = (I_{3.60}/3) \times 100.1/(I_{7.35-8.15}/7) + 271.5 \quad (\text{S2})$$

where 100.1 and 271.5 are the molecular weights of MMA and CPDN, respectively. The molecular weights of PMMA sample calculated from the 1H NMR spectrum ($M_{n,NMR}$) was 8300 g/mol, which was close to the SEC value (7700 g/mol), indicating that the PMMA was end-capped by CPDN species with high fidelity ($F_n = 92.7\%$). The chemical shifts at about

0.83, 1.01, and 1.22 ppm (^1H NMR) were ascribed to syndiotactic (*rr*), atactic (*mr*), and isotactic (*mm*) methyl groups, respectively. The tacticity of PMMA obtained in the presence of CPDN and $\text{Mn}(\text{acac})_3$ was calculated with 7.9% *mm*, 31.6% *mr* and 60.5% *rr* triads, which agreed with the tacticity distribution for common radical polymerization of MMA, confirming further that the polymerization was via a radical-mediated mechanism.

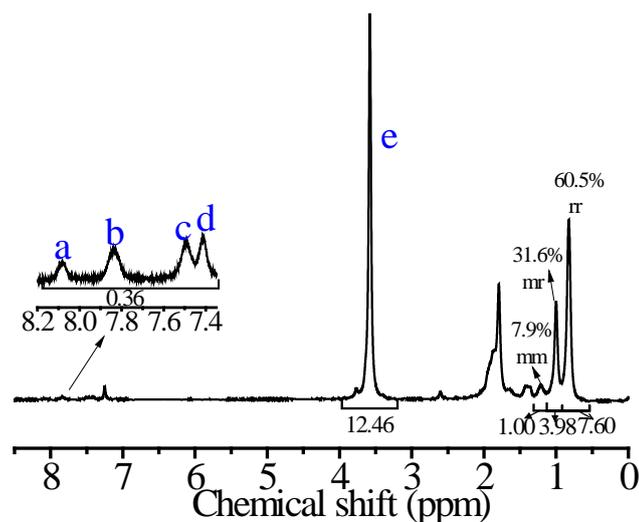


Figure S10. ^1H NMR spectrum of PMMA ($M_{n,\text{SEC}} = 7700$ g/mol, $M_w/M_n = 1.20$) obtained in the presence of CPDN and $\text{Mn}(\text{acac})_3$ with CDCl_3 as the solvent and tetramethylsilane (TMS) as the internal standard. Polymerization conditions: $[\text{MMA}]_0/[\text{CPDN}]_0/[\text{Mn}(\text{acac})_3]_0 = 200/2/1$, MMA = 1.0 mL, DMSO = 0.5 mL; time = 8 h, conversion = 34.9%; temperature = 25 °C.

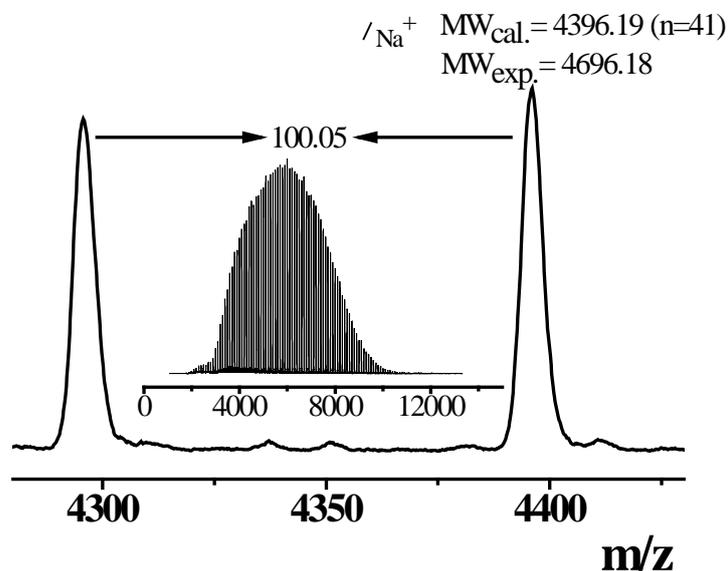
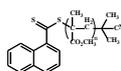


Figure S11. Matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry of poly(methyl methacrylate) (PMMA, $M_{n,SEC} = 7700$, $M_w/M_n = 1.23$) from $Mn(acac)_3$ initiated RAFT polymerization of MMA.

Table S1. Control polymerizations of MMA under various conditions.

Entry ^a	Polymerization Condition	Time (h)	Conv. (%)	$M_{n,SEC}$ (g/mol)	M_w/M_n	$M_{n,th}$ (g/mol)
1	$[MMA]_0/[CPDN]_0 = 200/1$	120	0	--	--	--
2	$[MMA]_0/[CPDN]_0/[AIBN]_0 = 200/1/1$	96	56.4	22300	1.09	11500
3	$[MMA]_0/[Mn(acac)_3]_0 = 200/1$	2	21.4	135000	1.55	--
4		3	38.6	135300	1.67	--
5 ^b	$[MMA]_0/[CPDN]_0/[Mn(acac)_3]_0 = 200/1/1$	24	23.4	12400	1.13	5000
6 ^b		34	63.6	17100	1.12	13000

^a) Polymerization conditions: MMA = 1.0 mL, solvent = 0.5 mL, temperature = 25 °C, DMSO; ^b) DMF.

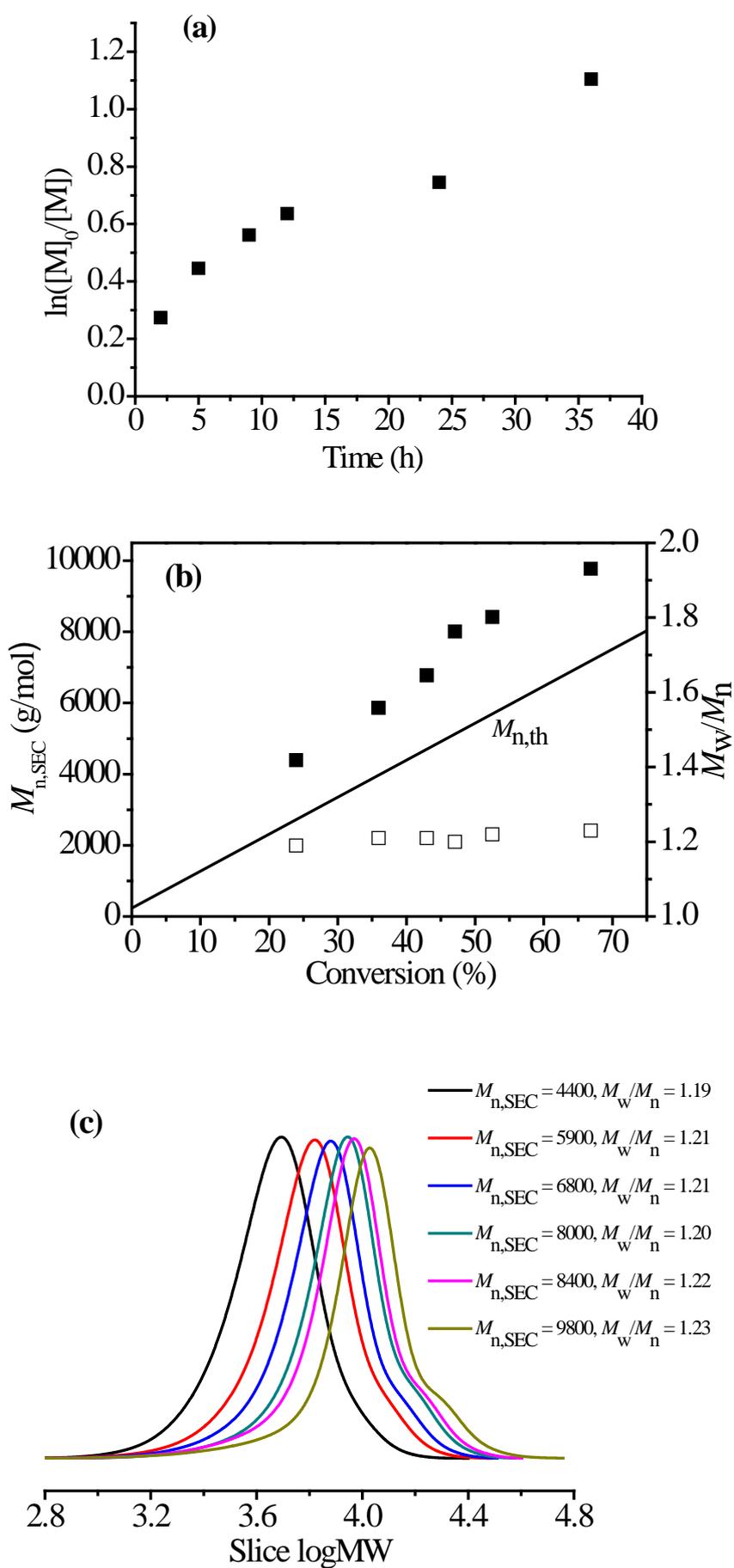


Figure S12. (a) Kinetic investigation ($\ln([M]_0/[M])$ versus time) (b) Dependence of $M_{n,SEC}$ and M_w/M_n on the conversion (c) Evolution of SEC traces of the bulk polymerization of St initiated by $Mn(acac)_3$ with BTCD as RAFT agent. St = 1.0 mL, $[St]_0/[Mn(acac)_3]_0/[BTCD]_0 = 200/1/2$, Temperature = 100 °C. BTCD = benzyl 4H-1,2,4-triazole-4-carbodithioate. $[M]_0$ and $[M]$ refer to the initial concentration and instant concentration of St, respectively. $M_{n,th} = ([St]_0/[BTCD]_0) \times M_{st} \times \text{Conversion} + M_{BTCD}$, where M_{st} and M_{BTCD} represent the molecular weights of St and BTCD, respectively.

1. Z. B. Zhang, X. L. Zhu, J. Zhu, Z. P. Cheng, S. P. Zhu, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 3343–3354.