

Supplementary Information

Cobalt(III) Acetylacetonate Initiated RAFT Polymerization of Acrylonitrile and Its Application in Removal of Methyl Orange after Electrospinning

Yuanyuan Xu, Jinming Sun, Hou Chen*, Liangjiu Bai

School of Chemistry and Materials Science, Ludong University, Yantai 264025, China

Typical procedures for RAFT polymerization of AN

The monomer (AN, 1.00 mL, 15.19 mmol), solvent (DMF, 1.00 mL), initiator (Co(acac)₃, 27.06 mg, 0.0760 mmol), and chain transfer agent (CPDN, 1.0 mg, 0.0036 mmol) were put into a 5 mL ampule in the following order: Co(acac)₃, CPDN, AN and DMF. The solution was deoxygenated with three freeze-pump-thaw cycles. The ampule was flame sealed and placed in DF-101S oil bath equipped with magnetic stirrer thermostat at 90 ± 0.2 °C. Then the ampule was cooled in ice water after a certain time. Then it was opened and content in ampule was adequately dissolved in 5-8 mL DMF. Afterwards, the solution was precipitated into 150 mL methanol with stirring. The polymer was isolated via filtration and dried under vacuum until the constant weight was recorded at ambient temperature. The monomer conversion was determined by gravimetric calculation. The obtained polymers were used for GPC characterization and electrostatic spinning.

Chain extension using PAN as the macroinitiator

The PAN sample ($M_{n, GPC} = 74500$, $M_w/M_n = 1.31$) was selected to be the macroinitiator, obtained under the condition of $[AN]_0:[Co(acac)_3]_0:[CPDN]_0 = 200:1:0.05$, and AN:DMF = 1:1 (V/V) after 12 h. The polymerization was proceeded with molar ratios of $[AN]_0:[PAN]_0:[Co(acac)_3]_0 = 500:0.1:1$, and AN:DMF = 1:1 (V/V) at 90 ± 0.2 °C for 12 h. The rest procedures were identical to those mentioned above.

Polymerization of AN mediated by Co(acac)₃-CPDN

As mentioned in the introduction, transition metals-mediated RDRP of AN are always a challenging topic. PAN was first successfully synthesized with Co(acac)₂ as the radical capping agent, rather than as the catalyst system. Here, Co(acac)₃ was neither catalyst nor end-capped agent. Polymerization of AN was investigated in the presence of Co(acac)₃ and CPDN at 90 °C. The behavior of polymerization, including polymerization rates and the "living" polymerization characteristics, was the main focus. Fig. S1 summaries the polymerization of AN with different concentrations of Co(acac)₃. The molar ratios of $[AN]_0:[Co(acac)_3]_0:[CPDN]_0$ were 200:0.5:0.025, 200:1.0:0.025, and 200:1.5:0.025, respectively, keeping the usage of CPDN constant. As can be seen from Fig. S1 that the polymerization proceeded smoothly and the kinetics plots were pseudo first-order linear ones ($\ln([M]_0/[M]) = k_p[R\cdot]t$), indicating that the number of radicals was constant and occurrence of irreversible transfer reactions or termination could be neglected. It is a typical manifestation of

"living"/controlled radical polymerization. The polymerization rate was slightly lowered with the declining concentration of $\text{Co}(\text{acac})_3$. The AN monomer conversion was obviously increasing with an increase amount of $\text{Co}(\text{acac})_3$. To further investigate the initiator role of $\text{Co}(\text{acac})_3$, the polymerization experiments were conducted in the absence and trace amounts of $\text{Co}(\text{acac})_3$, respectively, as shown in Table TS1 (entries 1, 2, 3). There was no monomer conversion even the reaction lasted long enough due to the lack of initiating radicals and insufficiently initiated ability, respectively. Compared with entries 4, 5, 6, and 7 in Table TS1, relatively higher monomer conversion was obtained with the increasing concentration of $\text{Co}(\text{acac})_3$ for more initiating radicals generation into the reaction system. The phenomena further conformed the role of $\text{Co}(\text{acac})_3$ as the initiator. Fig. S2 describes the number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) versus AN monomer conversion at different feed ratios of $\text{Co}(\text{acac})_3$. The molecular weights of PAN increased linearly with monomer conversion and the molecular weight distributions ($M_w/M_n < 1.46$) kept narrow in all cases. All the evidence shows that the polymerization proceeded in a controlled manner mediated by $\text{Co}(\text{acac})_3$ and CPDN.

The effect of CPDN concentrations on the polymerization was investigated as well. The molar ratio of $[\text{AN}]_0:[\text{Co}(\text{acac})_3]_0$ was kept 200:1. It was found from Fig. S3 that the polymerization proceeded smoothly in all cases (here, the polymerization results of $[\text{AN}]_0:[\text{Co}(\text{acac})_3]_0:[\text{CPDN}]_0 = 200:1:0.05$ and $\text{AN:DMF} = 1:1$ (V/V) were repeatedly illustrated for a better comparison). The polymerization rate was slightly

lowered as the concentration of CPDN increased from $[AN]_0:[Co(acac)_3]_0:[CPDN]_0 = 200:1:0.05$ through $200:1:0.10$ to $200:1:0.15$. To further demonstrate the inhibition of CPDN, the polymerization was conducted in the absence of CPDN (Table TS2: entries 1-3). The monomer conversion increased rapidly compared with those in entries 4-6 (Table 2). When the molar ratio of $[AN]_0:[CPDN]_0$ reached $200:0.2$ (Table TS2: entry 7), the conversion was obviously lowered. The phenomena were in accordance with the RAFT polymerization mechanism that retard would occur when the chain transfer agent was used in a high degree. Fig.S4 shows that the M_n increased linearly with AN monomer conversion and the M_w/M_n were below 1.50 for all the cases. However, in the absence of CPDN (entries 1-3), the M_n was out of control and M_w/M_n was as high as 1.61. The higher concentration of CPDN was (entries 4-7), the better control of polymerization over M_n and M_w/M_n would exhibit. The above results demonstrate that the polymerization in the presence of $Co(acac)_3$ -CPDN was most probably via a RAFT process with $Co(acac)_3$ as the initiator and CPDN as the RAFT agent. The polymerization mechanism was illustrated in Scheme 1.

Chain extension of PAN with PAN as the macroinitiator

The living nature of the polymer was further conformed by chain extension upon the addition of fresh AN monomer. The PAN sample ($M_n = 74500$, $M_w/M_n = 1.31$) was used as the macroinitiator. The chain extension was successful with $Co(acac)_3$ as the initiator, and PAN with much higher molecular weight ($M_n = 133200$) and narrow molecular weight distribution ($M_w/M_n = 1.39$) was obtained. It was clear from the

result that most of the end groups of the polymer were active for participation in chain extension reaction.

Entry ^a	conditions	Concentrations (mmol.L ⁻¹)	t/h	Conv. (%)	M_n (g.mol ⁻¹)	M_w/M_n
1	No radical source	--	24	0	--	--
2	No radical source	--	120	0	--	--
3	Co(acac) ₃ = 0.05 equiv.	1.90	72	0	--	--
4	Co(acac) ₃ = 0.1 equiv.	3.80	48	16.13	143700	1.28
5	Co(acac) ₃ = 1.0 equiv.	37.98	8	20.40	69000	1.46
6	Co(acac) ₃ = 1.0 equiv.	37.98	12	33.65	74500	1.31
7	Co(acac) ₃ = 1.0 equiv.	37.98	24	79.34	81600	1.34

^apolymerization conditions: AN = 1 mL, AN = 200 equiv., CPDN = 0.05 equiv.,
C_(CPDN) = 1.90 mmol.L⁻¹, temperature = 90 °C.

Table TS1. The control ability of initiators under various conditions

Entry ^b	conditions	Concentrations (mmol.L ⁻¹)	t/h	Conv. (%)	M_n (g.mol ⁻¹)	M_w/M_n
1	Free of CPDN	--	4	20.36	80500	1.56
2	Free of CPDN	--	12	70.67	89600	1.61
3	Free of CPDN	--	24	90.78	123500	1.57
4	CPDN = 0.05 equiv.	1.90	8	20.40	69000	1.46
5	CPDN = 0.10 equiv.	3.80	8	15.01	55500	1.44
6	CPDN = 0.15 equiv.	5.70	12	13.42	38100	1.45
7	CPDN = 0.20 equiv.	7.60	36	7.57	37600	1.42

^bpolymerization conditions: AN = 1 mL, AN = 200 equiv., Co(acac)₃ = 1.0 equiv.,

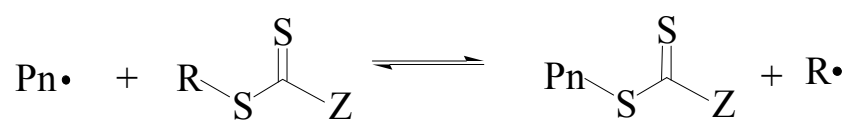
$C_{\text{Co(acac)}_3} = 37.98 \text{ mmol.L}^{-1}$, temperature = 90 °C.

Table TS2. The control ability of CPDN under various conditions

Initiation



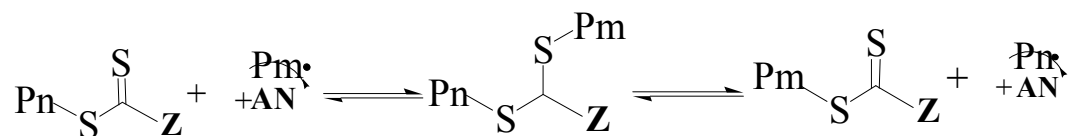
Reversible chain transfer



Re-initiation



Chain equilibration



Termination



Scheme 1: Proposed mechanism of $\text{Co}(\text{acac})_3$ -mediated polymerization of AN controlled by CPDN.

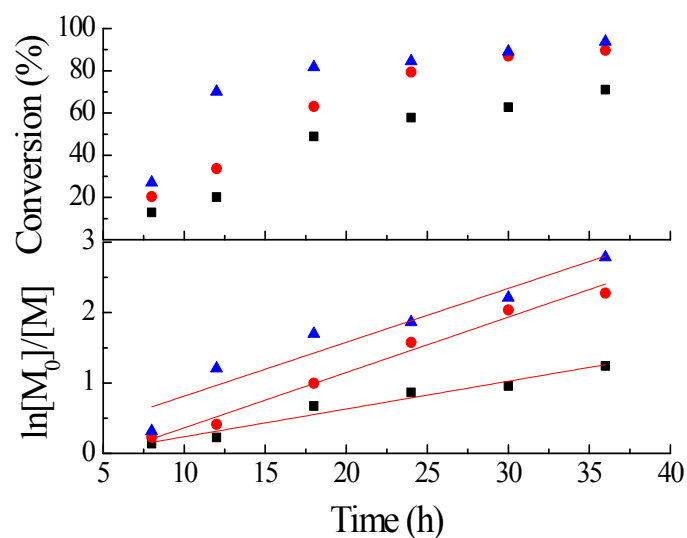


Fig. S1: Kinetics investigation ($\ln([M]_0/[M])$ and conversion versus time) with different concentrations of $\text{Co}(\text{acac})_3$, wherein $[M]_0$ and $[M]$ were the initial and final monomer concentration, respectively. All the experiments were conducted with $\text{AN}:\text{DMF} = 1:1$ (V/V).

■ $[\text{AN}]_0:[\text{Co}(\text{acac})_3]_0:[\text{CPDN}]_0 = 200:0.5:0.05$,

● $[\text{AN}]_0:[\text{Co}(\text{acac})_3]_0:[\text{CPDN}]_0 = 200:1.0:0.05$,

▲ $[\text{AN}]_0:[\text{Co}(\text{acac})_3]_0:[\text{CPDN}]_0 = 200:1.5:0.05$

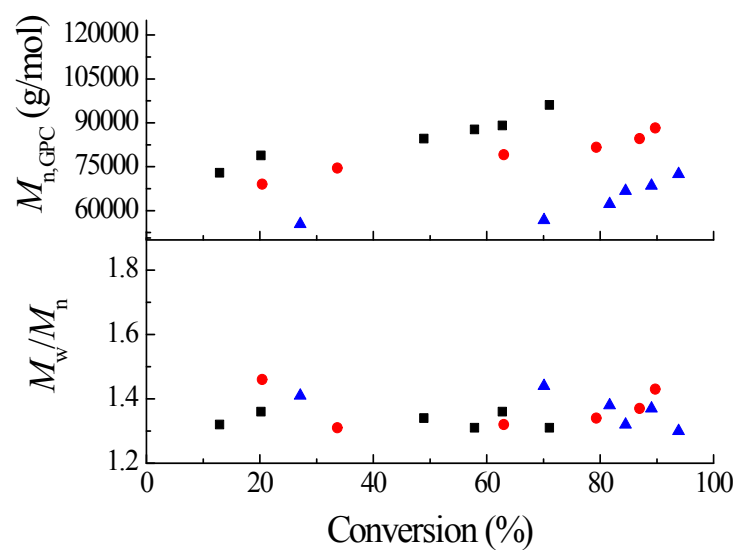


Fig. S2: The number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) of obtained PAN from RAFT polymerization as a function AN monomer conversion under various molar ratios of $[AN]_0/[Co(acac)_3]_0$. All the experiments were conducted with AN:DMF = 1:1 (V/V). (■ $[AN]_0:[Co(acac)_3]_0:[CPDN]_0 = 200:0.5:0.025$, ● $[AN]_0:[Co(acac)_3]_0:[CPDN]_0 = 200:1.0:0.025$, ▲ $[AN]_0:[Co(acac)_3]_0:[CPDN]_0 = 200:1.5:0.025$)

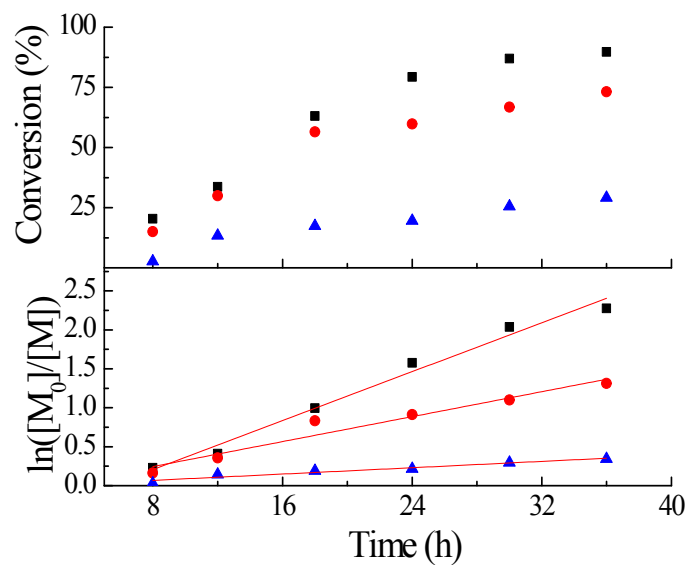


Fig. S3: Kinetics investigation ($\ln([M]_0/[M])$) and conversion versus time (t) with different concentration of CPDN, wherein $[M]$ represent the concentration of monomer. All the experiments were conducted with AN:DMF = 1:1 (V/V).

■ $[AN]_0:[Co(acac)_3]_0:[CPDN]_0 = 200:1:0.05$,

● $[AN]_0:[Co(acac)_3]_0:[CPDN]_0 = 200:1:0.1$,

▲ $[AN]_0:[Co(acac)_3]_0:[CPDN]_0 = 200:1:0.15$

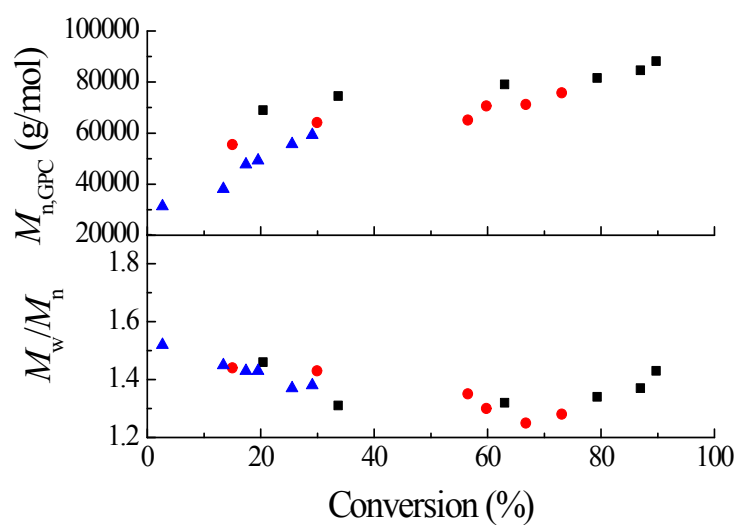


Fig. S4: The number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) of obtained PAN from RAFT polymerization versus conversion under various molar ratios of $[AN]_0/[CPDN]_0$. All the experiments were conducted with AN:DMF = 1:1 (V/V).

■ $[AN]_0:[Co(acac)_3]_0:[CPDN]_0 = 200:1:0.05$,

● $[AN]_0:[Co(acac)_3]_0:[CPDN]_0 = 200:1:0.1$,

▲ $[AN]_0:[Co(acac)_3]_0:[CPDN]_0 = 200:1:0.15$