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Living radical polymerization of vinyl acetate mediated by iron(III) acetylacetonate in the presence of a reducing agent

Jirong Wang,[a] Jun Zhou,[a] Hussameddin S. E. M. Sharif,[a] Dan He,[b] Yun Sheng Ye,[a] Zhigang Xue*[a] and Xiaolin Xie[a]

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Iron(III) acetylacetonate ($Fe(acac)_3$) was employed to mediate the controlled radical polymerization of vinyl acetate (VAc) in the presence of a reducing agent (RA). Polymerizations were conducted with a molar ratio of $[VAc]_0/[initiator]_0/[Fe(acac)_3]_0/[RA]_0/[ligand]_0 = 500 : 0.8 : 1 : 2 : 3$ and a volume ratio of VAc/solvent = 1 at 70 °C to investigate the effects of initiator, solvent, and reducing agent on the polymerization reaction. The kinetic plots of VAc polymerizations were linear, and the molecular weights (M_n) increased proportionately with monomer conversions.

Introduction

Polymeric materials have been widely used in everyday life, and nearly half of all polymers are produced by conventional radical polymerization.[1,2] However, it is essentially impossible for conventional radical polymerization to obtain macromolecules with a certain structure, predetermined molecular weight (M_n) as well as narrow molecular weight distributions (MWDs) because of the short lifetime of the reactive radical intermediates, termination and chain transfer reactions. Thus, a series of controlled/"living" radical polymerization methods like nitroxide mediated radical polymerization (NMP),[3–5] atom transfer radical polymerization (ATRP),[6–12] and reversible addition–fragmentation chain transfer (RAFT) polymerization[13–15] were developed rapidly. Those methods are applicable to many monomers including styrenics, (meth)acrylates, (meth)acrylamides, acrylonitrile, and several other monomers, through establishing a dynamic equilibrium between dormant species and a low concentration of propagating radicals.

However, one of the ultimate difficulties in the field of radical polymerization is the possibility to control the polymerization of less reactive monomers (*e.g.* vinyl esters, vinyl acetate, vinyl chloride, other halogenated olefins, and simple alkenes).[16–28] The organometallic mediated radical polymerization (OMRP)[29–36] is a "reversible deactivation" method, and this technique can achieve controlled growth for less reactive monomers that are associated to more reactive radicals just by generating a $P_n–M_t^{x+1}/L_y$ dormant species with a homolytically weak metal–carbon bond. Compared with other inorganic transition catalysts, organocatalysts are usually oil-soluble, which makes them possible to conduct the polymerization in homogeneous conditions without solvent. Up to date, many complexes such as Mo,[37–40] Cr,[41,42] Os,[43,44] and V[45–47] have been used in OMRP. To the best of our knowledge, cobalt-mediated radical polymerization (CMRP)[48] is the most commonly used subcategory of OMRP, and it can produce polymers with relatively predetermined M_n and narrow MWDs.

Recently, much attention has been paid to the concept of green chemistry, and the searching for environmentally friendly solvents and catalysts represents both opportunities and challenges. Organoiron complexes are one of the most promising trapping agents for OMRP.[49–53] In comparison to other organometallics, iron-based complexes are relatively less toxic and more bio-compatible for biomedical applications. Very recently, Poli *et al.*[49] studied radical polymerization of vinyl acetate (VAc) moderated by iron(II) acetylacetonate ($Fe(acac)_2$) by an OMRP method. The metal–carbon bond of $(acac)_2Fe–PVAc$ formed in the process of polymerization is homolytically fragile, which is the key factor in controlling the polymerization of VAc. However, $Fe(acac)_2$ is very easy to be oxidized when exposure to air, and therefore, it needs to be saved under a dry inert atmosphere,[54] which will affect the practical application of $Fe(acac)_2$ as a trapping agent for OMRP.

The problem with the sensitivity of lower oxidation state metals to air and humidity becomes more and more intolerable for metal-mediated living radical polymerization. In contrast, the facile preparation, storage, handling method, and the ability to conduct under low catalyst concentration make higher oxidation state iron-based catalysts receive much concern. The activators generated by electron transfer for ATRP (AGET ATRP)

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[a] *Key Laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China. E-mail: zgxue@mail.hust.edu.cn; Fax: +86 27 87543632; Tel: +86 27 87793241*

[b] *Key Laboratory of Optoelectronic Chemical Materials, Devices of Ministry of Education, School of Chemical and Environmental Engineering, Jianghan University, Wuhan 430056, China*

that employs higher oxidation state iron-based catalysts has gained a significant progress on account of its easy operation and better control over the polymerization.[12,55–58] Very recently, our group investigated the iron(III)-mediated AGET ATRP of methyl methacrylate (MMA), using polar solvents (NMP, DMF, CH_3CN) as ligands, tin(II) 2-ethylhexanoate ($Sn(EH)_2$)[59] and some alcohols[60,61] as the reducing agents. These systems yield polymers with relatively low M_w/M_n values and well-controlled molecular weights. In 2014, Zhang and Cheng[62] reported bulk AGET ATRP of MMA using iron(III) acetylacetonate ($Fe(acac)_3$) as a catalyst, and the results indicated good features of living radical polymerization with MWDs around 1.2. Turning our attention to OMRP, we raise a very significant hypothesis similar to AGET ATRP, by using high oxidation iron-based complex and adding reducing agent to this system. The trapping agent of OMRP will be produced *in situ* to improve the polymerization of less reactive monomers.

In this study, we investigated the $Fe(acac)_3$-mediated radical polymerization of VAc in the presence of ascorbic acid (AsAc) as reducing agent. The effects of different ligands and reducing agents on polymerizations were discussed. In addition, solution OMRP of VAc was also performed with toluene as solvent.

Experimental

Materials

Vinyl acetate (VAc, 98+%, Sinopharm) was passed through a column filled with natural alumina, dried over calcium hydride (CaH_2), distilled under reduced pressure, and stored in a freezer under argon. Pyridine (py, 99.5%, Sinopharm) and triethylamine (TEA, 99%, Sinopharm) were also dried over CaH_2 and distilled under reduced pressure. 2,2′-Azobisisobutyronitrile (AIBN, 98%, Sinopharm) was recrystallized in ethanol. Iron(III) acetylacetonate ($Fe(acac)_3$, 99.95%, Aldrich), Zn^0 (wire, diameter 1.0 mm, 99.95%, Alfa Aesar), Fe^0 (wire, diameter 1.0 mm, 99.99%, Alfa Aesar), methanol (99+%, Sinopharm), ethanol (99+%, Sinopharm), ascorbic acid (AsAc, 99+%, Sinopharm), ethylene glycol (EG, 99+%, Sinopharm), glycerol (99+%, Sinopharm), and triphenyl phosphine (TPP, 99+%, Sinopharm) were used without further purification.

Polymerization procedures

A Schlenk flask (25 mL) was charged with $Fe(acac)_3$ (76.4 mg, 0.216 mmol), AIBN (28.4 mg, 0.173 mmol), AsAc (76.2 mg, 0.432 mmol), and TPP (170 mg, 0.649 mmol). The flask was sealed with a rubber septum and was cycled three times between vacuum and nitrogen to remove oxygen. Degassed VAc (10 mL, 108.1 mmol) was then added to the flask through degassed syringes. The solution was stirred for 20 min at room temperature. After three freeze–pump–thaw cycles, the flask was immersed in a thermostated oil bath at 70 °C. In solution polymerization, all the components were dissolved in toluene and stirred in oil bath at 70 °C for 40 min, then the monomer was added. At timed intervals, samples were withdrawn from the flask with a degassed syringe. The monomer conversion was determined gravimetrically after removal of the unconverted monomer under reduced pressure, and the resulting residue was precipitated in heptane, dried, used for gel permeation chromatograph (GPC) characterization.

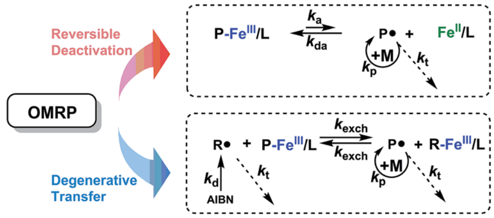
Measurement

The number-average molecular weight ($M_{n,GPC}$) and M_w/M_n of the polymers were determined using Agilent 1100 GPC using PL gel 79911GP-104 (7.5 × 300 mm, 10 μm beads' size) column. THF was used as the eluent at a flow rate of 1 mL min^{-1} at 35 °C. Linear polystyrene standards were used for calibration. The ^1H NMR spectrum was obtained on a Burker AV400 NMR spectrometer using deuterated dimethyl sulfoxide (DMSO-d_6) or $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard at ambient temperature. The UV spectrum was obtained on a Evolution 220 UV-Visible Spectrophotometer using *N*,*N*-dimethylformamide as the solvent at ambient temperature.

Results and discussion

As mentioned above, $Fe(acac)_2$ was shown to insure the controlled growth of VAc by OMRP in spite of some deviation from the theoretically predicted molecular weight.[49] The mechanism of iron-based catalyst mediated radical polymerization may be possible by direct dissociative bond breaking (Scheme 1), or by degenerative transfer if an independent radical source is available and if the metal coordination sphere allows it (Scheme 1).

Besides, combining all kinds of advantages of AGET ATRP involved in the introduction, we tested the similar system just using reducing agent and $Fe(acac)_3$ together to polymerize VAc. First, as a very cheap and available thermal initiator, AIBN was used to initiate the normal radical polymerization of VAc under the condition of VAc/AIBN = 500 : 0.8 at 70 °C in bulk (Table 1, entries 1 and 2). The polymerization approached 43.8% monomer conversion just in 25 min with a large viscosity (entry 2). The molecular weight distribution was extremely broad ($M_w/M_n = 2.35$) and a high molecular weight was also obtained (M_n = 281 700), which was the typical character of radical polymerization due to the existence of bimolecular termination. To probe the effect of $Fe(acac)_3$ in the polymerization process, the polymerizations were proceeded in bulk with a $Fe(acac)_3$/AIBN ratio of 0.8 and a [VAc]/[$Fe(acac)_3$] ratio of 500 (entries 3 and 4). Undoubtedly, it does not belong to the category of controlled polymerization. However, it is interesting to find that the rate of polymerization was slowed down and the molecular



Scheme 1 Mechanism of OMRP.

Table 1 Radical polymerization of VAc mediated by $Fe(acac)_3$[a]

Entry	$Fe(acac)_3$	TPP	RA	Time (h)	Conv. (%)	$M_{n,th}$[b] ($g\ mol^{-1}$)	$M_{n,GPC}$ ($g\ mol^{-1}$)	M_w/M_n
1	No	No	No	0.33	15.3	NA	260 100	1.98
2	No	No	No	0.42	43.8	NA	281 700	2.35
3	Yes	No	No	1.50	14.1	NA	108 900	2.30
4	Yes	No	No	2.25	49.4	NA	111 500	2.42
5	Yes	No	Yes	1	10.0	4300	45 800	1.72
6	Yes	No	Yes	2	21.6	9280	48 800	1.79
7	Yes	No	Yes	5	37.8	16 250	53 700	1.92
8	Yes	Yes	Yes	1.5	10	4300	38 200	1.65
9	Yes	Yes	Yes	4.5	29.2	12 500	49 900	1.78
10	Yes	Yes	Yes	10.5	47.1	20 200	52 300	1.56
11	Yes	Yes	No	1	14.0	6020	107 400	2.25
12	Yes	Yes	No	2.40	54.8	23 500	125 600	2.30

[a] $[VAc]_0/[Fe(acac)_3]_0/[AIBN]_0/[AsAc]_0/[TPP]_0 = 500:1:0.8:2:3$, 70 °C. [b] $M_{n,th} = ([VAc]_0/[Fe(acac)_3]_0) \times M_{VAc} \times$ conversion, M_{VAc} represents the molecular weight of VAc.

weight was lower than that obtained from conventional radical polymerization, which may be due to its inhibition effect and the reducibility of radicals dissociated from AIBN.

Subsequently, the reducing agent (AsAc) was added into the polymerization system. The reaction was performed with each component ratio of $[VAc]/[Fe(acac)_3]/[AIBN]/[AsAc] = 500:1:0.8:2$, and the polymerization was expectedly much slower, reaching 49.2% conversion in 6.5 h. It is noteworthy that the MWDs and molecular weights were much smaller in the presence of reducing agent (entries 5–7). The phenomenon gradually closed to a living polymerization and indicated that the reducing agent (AsAc) indeed had an effect on $Fe(acac)_3$. However, the results also stated that the ability of $Fe(acac)_2$ to trap and reversibly release the growing PVAc radical chains was not fully brought to play a certain role. In other words, only a small fraction of the iron centers was operating as chain growth mediators. In order to further improve the controllability of polymerization, the effect of ligand was then taken into consideration with a $[TPP]/[Fe(acac)_3]$ ratio of 3 : 1, while maintaining all other parameters unchanged. The results, shown in Table 1 (entries 8–10), demonstrated that the TPP system provided a much lower rate of polymerization (47.1% in 10.5 h), and a relatively lower MWD, even though the observed M_n values of these polymers were again much greater than expected. It proved that the system with both reducing agent and ligand is practicable to polymerize the VAc. In the end, the polymerization was conducted to explore the effect of TPP in the absence of AsAc. The phosphorus ligands were usually used as ligands[63–69] as well as reducing agents[70] in ATRP. However, the results revealed that the reducing reaction of TPP and $Fe(acac)_3$ was not too strong (entries 11 and 12).

Effect of initial concentration of AIBN

To investigate the detailed polymerization behaviors of iron(III)-mediated OMRP using $Fe(acac)_3$, the effect of different initial concentrations of AIBN was taken into account. As already confirmed, keeping a suitable concentration of free radical initiator is critical to the polymerization of VAc since it dominates the radical concentration during the polymerization. Then the VAc polymerizations were carried out with different initial concentrations of AIBN at 70 °C. The results are illustrated in Fig. 1.

As shown in Fig. 1, the polymerization process was speeded up in degrees with the increase of initial concentration of AIBN. When the AIBN/Fe ratio reached to 4, the slope became very steep and a extremely large polymerization rate was obtained.

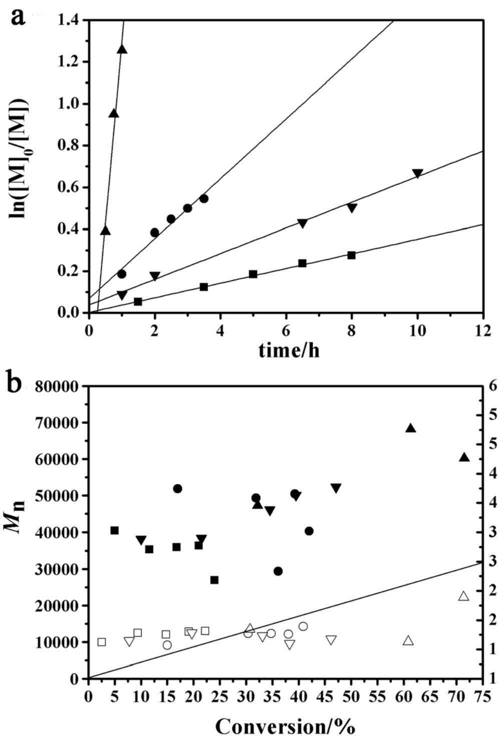


Fig. 1 (a) Kinetic plots of $\ln([M]_0/[M])$ *versus* time and (b) plots of M_n (filled symbols) and M_w/M_n (open symbols) values *versus* conversion for $Fe(acac)_3$-mediated OMRP of VAc. $[VAc]_0/[Fe(acac)_3]_0/[AIBN]_0/[AsAc]_0/[TPP]_0 = 500:1:x:2:3$, 70 °C. ■: $x = 0.6$; ▼: $x = 0.8$; ●: $x = 1.2$; ▲: $x = 4$.

Combining the observed M_n and MWDs (~1.5), the most suitable ratio of AIBN/Fe was 0.8. The 0.8 equiv. of AIBN, generating in principle 1.6 equiv. of primary radicals, effectively affords a nearly stoichiometric amount of initiating chains once the initiator efficiency is taken into account. The conversion increased linearly and rapidly, indicating the control mechanism of reversible deactivations. The molecular weights were higher than theoretical ones, which may be due to the slow reducing process of AsAc and Fe(III), while during this time, the radicals isolated from AIBN initiated the polymerization of VAc.

Effect of VAc concentration

As shown in Table 2, different molar ratios of [VAc]/[Fe(acac)$_3$] of 300, 500, 800, 1200 were designed, and monomer conversions in 4 h and 10 h were achieved, respectively (58.2%, 48.9%, 36.8%, 18% in 10 h). The decreased polymerization rate may be due to the low radical concentration. With increasing the molar ratio, the controllability gradually became poor (higher M_n and MWDs).

Effect of different ligands

In Co(acac)$_2$-mediated VAc polymerization system, the controlled polymerization without ligand only occurred by degenerative transfer process in the presence of excess radicals, while the reactions including ligand also involved the reversible release of the growing PVAc radicals.[71] The addition of coordinating ligands such as py, TEA, and H_2O provided faster polymerizations relative to the ligand-free system. However, the opposite result was obtained when the coordinating ligands were added into Fe(acac)$_2$-mediated VAc polymerization system, with which the polymerization was slowed down by the presence of Lewis bases.[49] The addition of ligand (L) makes Co(acac)$_2$ combine with two molecules L and form Co(acac)$_2$(L)$_2$, meanwhile, the PVAc–Co^{III}(acac)$_2$ dormant species can only join one L to form PVAc–Co^{III}(acac)$_2$(L), of which stability is greater poor than the former. While for Fe system, the ability of Lewis base to stabilize the Fe^{III} dormant species is much better than the trapping agent Fe(acac)$_2$. Thus it can be seen that the type and amount of the ligand have an important effect on different polymerization systems. The effect of different ligands was also studied (Table 3). TPP, TEA, and py were respectively used as the ligand and the polymerization was conducted with a ratio of [VAc]$_0$/[Fe(acac)$_3$]/[AIBN]/[AsAc]/[L] = 500 : 1 : 0.8 : 2 : 3.

Table 3 Effect of ligands on OMRP of VAc[a]

Entry	Ligand	Time (h)	Conv. (%)	$M_{n,th}$ (g mol^{-1})	$M_{n,GPC}$ (g mol^{-1})	M_w/M_n
1	TPP	1.5	10	4300	38 200	1.65
2	TPP	4.5	29.2	12 500	49 900	1.78
3	TPP	10.5	47.1	20 200	52 300	1.56
4	py	20	20.0	8600	161 000	1.64
5	py	31	22.4	9630	148 500	1.78
6	TEA	4.5	14.5	6200	37 600	1.79
7	TEA	8.5	21.2	9100	37 200	1.70
8	TEA	19.5	25.5	10 900	38 400	1.64

[a] $[VAc]_0/[Fe(acac)_3]_0/[AIBN]_0/[AsAc]_0/[L]_0 = 500 : 1 : 0.8 : 2 : 3$, 70 °C.

When TPP was used as the ligand, the polymerization rate was much faster than that obtained from py or TEA system. For instance, 47.2% monomer conversion can be obtained in 10.5 h (Table 3, entry 3), while only 22.4% and 25.5% of conversions (entries 5 and 8) could be achieved for py and TEA, respectively. The possible reason was that PPh_3 can form a relatively weaker binding to the reductive product of Fe(acac)$_3$. Meanwhile, the controllability was poor with high molecular weights and MWDs, especially for py and TEA systems.

Effect of different reducing agents

Similar to AGET ATRP, the reducing agent can continuously reduce the higher oxidized transition metal to lower transition metal activating species. Once the equilibrium established, then the polymerization was carried out in normal OMRP process. In this study, seven types of reducing agents were examined for the polymerization, *viz.* Fe^0, Zn^0, methanol, ethanol, EG, glycerol and AsAc, in conjunction with Fe(acac)$_3$ using AIBN as the initiator (Table 4). When using Fe^0 as the reducing agent, the system reacted quickly with a 38.8% conversion in 4.5 h, and the molecular weight and the PDI of the polymers were extremely large (entry 2), reaching up to 96 700 and 2.29, respectively. But for Zn^0 system, the polymerization became incredibly slower, and only 11.2% conversion was obtained in 31 h. What's more, the controllability reached the range of controlled polymerization with relative lower molecular weights and MWDs (entries 3–5). Comparing Fe^0 with Zn^0,

Table 2 Effect of the molar ratio of [VAc]/[Fe] on OMRP of VAc[a]

Entry	Fe	$[VAc]_0/[Fe]_0$	Time (h)	Conv. (%)	$M_{n,th}$ (g mol^{-1})	$M_{n,GPC}$ (g mol^{-1})	M_w/M_n
1	Fe(acac)$_3$	300	4	31.2	8050	25 600	1.75
			10	58.2	15 000	34 000	1.64
2	Fe(acac)$_3$	500	4	28.2	12 100	38 400	1.81
			10	49.8	21 000	49 600	1.58
3	Fe(acac)$_3$	800	4	16.7	11 400	45 600	1.91
			10	36.8	25 300	53 800	1.89
4	Fe(acac)$_3$	1200	4	10.1	10 400	62 200	1.93
			10	18	18 600	58 200	2.00

[a] $[VAc]_0/[Fe(acac)_3]_0/[AIBN]_0/[AsAc]_0/[TPP]_0 = x : 1 : 0.8 : 2 : 3$ (x = 300, 500, 800, 1200), 70 °C.

Table 4 Effect of reducing agent on OMRP of VAc[a]

Entry	RA	Time (h)	Conv. (%)	$M_{n,th}$ (g mol^{-1})	$M_{n,GPC}$ (g mol^{-1})	M_w/M_n
1	Fe^0	3	17.8	7650	89 000	2.33
2	Fe^0	4.5	38.8	16 680	96 700	2.29
3	Zn^0	8.5	6.1	2600	8200	1.37
4	Zn^0	19.5	8.8	3780	6070	1.67
5	Zn^0	31	11.2	4800	7020	1.47
6	Methanol	5	18.8	8080	52 600	1.70
7	Methanol	8	32.0	13 700	43 400	1.80
8	EG	4.5	28.6	12 300	48 200	1.85
9	EG	20.5	47.9	20 600	49 700	1.81
10	Ethanol	1.5	17.0	7310	91 800	2.04
11	Ethanol	3	41.7	17 900	82 200	2.22
12	Glycerol	3.5	10.1	860	68 200	1.64
13	Glycerol	5	10.4	4640	68 000	1.64
14	AsAc	1.5	10	4300	38 200	1.65
15	AsAc	4.5	29.2	12 500	49 900	1.78
16	AsAc	10.5	47.1	20 200	52 300	1.56

[a] $[VAc]_0/[Fe(acac)_3]_0/[AIBN]_0/[RA]_0/[TPP]_0 = 500:1:0.8:2:3$, 70 °C.

Zn^0 has a relatively strong reducing ability than Fe^0, which can be indicated by the negative standard electrode potentials (−0.76 V for Zn^{2+}/Zn, while −0.44 V for Fe^{2+}/Fe). Due to the existence of hydroxyl group, alcohol is generally used as reducing agent in AGET ATRP.[60,61] During the polymerization, ethanol was the fastest, and glycerol was the slowest with only 10.4% conversion in 5 h (entry 13). Integrated all aspects, relatively lower molecular weight and MWD were achieved by using AsAc as the reducing agent.

Subsequently, the effect of the amount of AsAc on polymerization was further studied, and the results were shown in Table 5. As we mentioned before, the polymerization without reducing agent run with a rapid rate and the results were out of the range of controlled polymerization (entries 1 and 2). When a small quantity of reducing agent was used in the polymerization, with the AsAc/Fe ratio of 0.2, 0.5, 0.8, respectively, the polymerization rate decreased with the increasing of AsAc content. The controllability is continuously getting better with a closer molecular weight and smaller PDI, from 2.25 to 1.69. However, when the AsAc/Fe ratio reached 1, 2 and 5, the polymerization rate presented the opposite results. Simultaneously, the increasing of reducing agent indeed improved the controllability of the polymerization system.

Table 5 Effect of the amount of AsAc on polymerization of VAc[a]

Entry	[AsAc]/[Fe]	Time (h)	Conv. (%)	$M_{n,th}$ (g mol^{-1})	$M_{n,GPC}$ (g mol^{-1})	M_w/M_n
1	0	1	14.0	6020	107 400	2.25
2	0	2	45.9	19 700	125 200	2.22
3	0.2	1.5	19.2	8200	58 700	2.14
4	0.2	3	42.1	18 100	74 200	2.12
5	0.5	1.5	13.7	5900	45 200	1.79
6	0.5	4.5	33.7	14 500	49 200	1.74
7	0.8	1.5	12.3	5290	37 800	1.69
8	0.8	6	33.1	14 200	38 300	2.28
9	1	2	14.6	6200	40 030	1.77
10	1	7.5	28.0	12 000	37 000	1.84
11	2	8	39.7	17 000	53 800	1.64
12	2	10	48.9	21 000	49 600	1.58
13	5	2	20.9	8980	48 800	1.62
14	5	4	33.1	14 200	34 300	1.80

[a] $[VAc]_0/[Fe(acac)_3]_0/[AIBN]_0/[AsAc]_0/[TPP]_0 = 500:1:0.8:x:3$ ($x = 0$, 0.2, 0.5, 0.8, 1, 2, 5), 70 °C.

Solution polymerization

After considering all the influence factors, the controllability of the polymerization system was still not perfectly improved. Then the polymerizations were carried out under more diluted conditions (50% v/v in toluene, see Table 6). All the components were first dissolved in the nonpolar solvent toluene and stirred in oil bath at 70 °C about 40 min, which contributes to a good dissolution and forming the deactivators (extra experiments with simultaneous adding of solvent and monomer were also implemented, and the results have no obvious difference with the former), then the monomer was added into the reaction flask. During the reaction process, the color gradually changed from original red to dark brown, and the polymerization was expectedly much slower than in bulk with only 40.2% conversion in 24 h. The existence of solvent resulted in an improved efficiency of $Fe(acac)_2$ which was generated by $Fe(acac)_3$ in the presence of AsAc. A greater proportion of iron centers appears to play a role in the moderation of chain growth in a more dilute solution. Even though the molecular weight values were once again higher than the theoretical one, both the molecular weight and MWDs were much smaller compared with the bulk polymerizations. Moreover, the controllability became better with the increased amount of reducing agent. However, the molecular weight almost unchanged even decreased as the conversion increased, presumably because of the formation of additional polymer chains by catalyzed chain transfer reactions.[49]

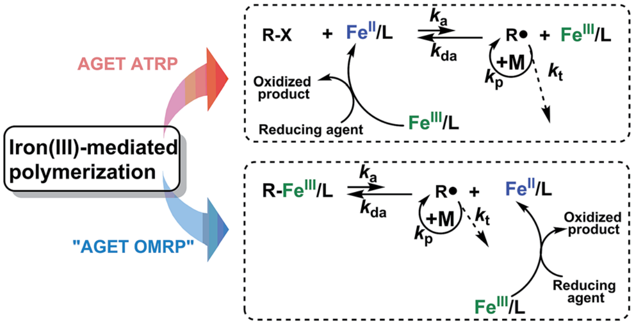
Polymerization mechanisms

In AGET ATRP, the higher oxidation state complex was firstly reduced into lower oxidation state by the reducing agent. Then alkyl halides, as the initiator of the system, combined with the

Table 6 Solution polymerization of VAc[a]

Entry	[AsAc]/[Fe]	Time (h)	Conv. (%)	$M_{n,th}$ (g mol^{-1})	$M_{n,GPC}$ (g mol^{-1})	M_w/M_n
1	0	1.5	20.1	8600	27 100	1.60
2	0	4.5	42.9	18 400	28 000	1.48
3	1	2.5	13.2	5670	19 800	1.45
4	1	18.5	34.6	14 800	20 500	1.48
5	2	4	20.9	8980	20 400	1.46
6	2	7	31.4	17 300	20 600	1.45
7	5	1.5	10.2	4390	20 900	1.37
8	5	7.5	24.5	10 500	19 400	1.42

[a] $[VAc]_0/[Fe(acac)_3]_0/[AIBN]_0/[AsAc]_0/[TPP]_0 = 500:1:0.8:x:3$ ($x = 0$, 1, 2, 5), 50% v/v in toluene.



Scheme 2 Mechanism of iron(III)-mediated living radical polymerization.

lower oxidation state metal complex to form high oxidation state metal complex and active radicals. After that, the reaction proceeded in a normal ATRP process and the AGET ATRP mechanism is shown in Scheme 2. Comparing to AGET ATRP, the plausible mechanism of organoiron(III)-mediated OMRP was shown in Scheme 2. At the beginning of polymerization, the whole system was Fe(III) atmosphere without any Fe(II), and the addition of reducing agent made the concentration of Fe(II) complexes increase continuously until establishing a dynamic equilibrium between the Fe(II) and Fe(III). Once the Fe(II) generated *in situ*, then the next process was similar to the normal OMRP.

The ^{1}H NMR spectra of the Fe(acac)$_2$ and Fe(acac)$_3$ revealed the redox reaction of Fe(acac)$_3$ and AsAc (Fig. 2). The Fe(acac)$_3$ is characterized by agreement with the coordinative saturation of the complex, at δ *ca.* 22 and −25. Their relative ratio agrees with their assignment to the CH$_3$ and CH protons, respectively. Fe(acac)$_2$ is very easy to be oxidized when exposure to air, and therefore, the commercially available Fe(acac)$_2$ showed the peak of Fe(acac)$_3$ at 22 ppm. Notably, the peak at 22 ppm was weakened in the presence of reducing agent (AsAc). In addition, UV-vis spectroscopy was also used to follow the transformation between Fe(III) and Fe(II) during the reducing process (Fig. 4). In the UV-vis spectrum of Fe(acac)$_3$, there is a weak and broad absorption at 430 nm, and a strong absorption at 272 nm owing to a combination of Fe(acac)$_3$ and AcacH (the absorption coefficient are 2.81 × 10^4 M^{-1} cm^{-1} and 9.44 × 10^3 M^{-1} cm^{-1}, respectively). While in Fe(acac)$_2$ (a), the absorption at 271 nm has weakened significantly, but there are also signals in 430 nm, which may ascribe to the purity of Fe(II) (even though the whole process was manipulated in glovebox). Then the reducing system with a same ratio in polymerization (Fe(acac)$_3$/AsAc = 2) was tested, the signal of Fe(III) became weaker with increasing time.

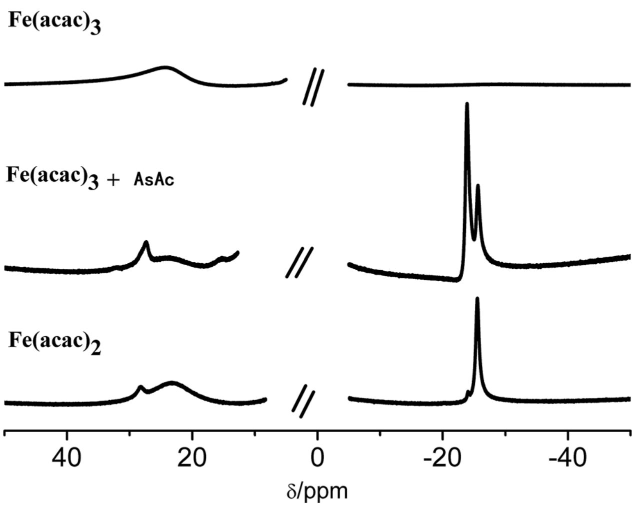


Fig. 2 Representative regions of the ^{1}H NMR spectra of Fe(acac)$_2$ and Fe(acac)$_3$ (DMSO-d_6).

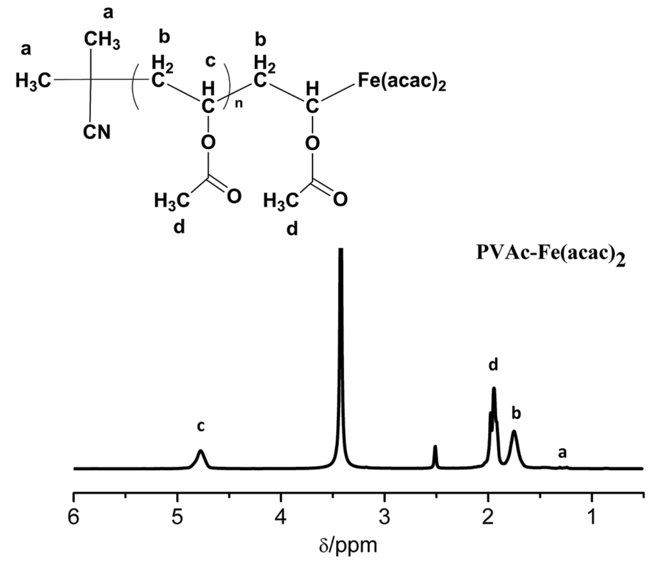


Fig. 3 ^{1}H NMR spectrum of iron adduct, PVAc–Fe(acac)$_2$ (DMSO-d_6).

Analysis of chain end and chain extension

The ^{1}H NMR of PVAc (see Fig. 3) confirmed the R$_0$-terminated PVAc, R$_0$ being the primary radical generated by AIBN. In addition to the signals characteristic of the PVAc protons (b–d), the R$_0$ signal was observed as resonance (a). In order to further confirm the livingness of the obtained polymer, a chain extension polymerization using PVAc ($M_{n,GPC}$ = 40 900, M_w/M_n = 1.68) as the macroinitiator was conducted. As shown in Fig. 5, there is a peak shift from the original polymer to the chain-

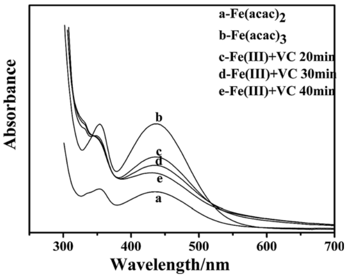


Fig. 4 (a) UV-vis spectrum of a 6.5 × 10^{-4} M Fe(acac)$_2$. (b) Fe(acac)$_3$. (c) Spectrum of reducing system with Fe(acac)$_3$/VC = 1 : 2 in different time.

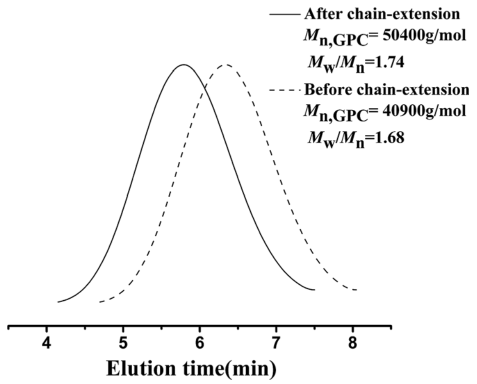


Fig. 5 GPC traces of PVAc before and after chain extension using PVAc prepared by $Fe(acac)_3$ system. Polymerization conditions: VAc/PVAc–$Fe(acac)_2$/PPh_3 = 800 : 1 : 3, V_{VAc} = 10 mL, in bulk, temperature = 70 °C.

extended PVAc with $M_{n,GPC} = 50\,400$, $M_w/M_n = 1.74$. These results verified the features of "living" or controlled polymerization of VAc using $Fe(acac)_3$ as the catalyst in reducing system, even though the activity of the macroinitiator was not high with a only 20% conversion after 15 h.

Conclusions

In conclusion, we described the OMRP of VAc controlled by $Fe(acac)_3$ by adding reducing agent. The polymerization process was slowed down by the addition of Lewis base, indicating a greater stabilization of the dormant PVAc–$Fe^{III}(acac)_2$ species relative to the trapping $Fe^{II}(acac)_2$ species by Lewis base coordination. Meanwhile, the Lewis base, TPP, slightly improved the controllability of the polymerization. The results are encouraging for a further exploration of higher oxidation state iron complexes and reducing agent as the controlling systems within the OMRP approach.

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