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Zero Valent Metal/RAFT Agent Mediated CRP of Functional Monomers at Room Temperature: a Promising Catalyst System for CRP

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In this work, zero-valent iron (Fe(0)) powder/RAFT agent was used as catalyst system for the control polymerization of glycidyl methacrylate (GMA) at ambient temperature (25 ^{o}C). A kinetic investigation indicated that the polymerization was a living/controlled process. Molecular weight increased linearly with monomer conversion with a relatively low molecular weight distribution (M_w/M_n < 1.35). Fe(0) wire or other zero valent metal powder (Co, Ni, Mn, Zn) are found to be applicable. Interestingly, polymeriztion of 4-vinylpyridine, 2-(dimethylamino)ethyl methacrylate or poly(ethylene glycol) monomethyl ether methacrylate can also be well controlled with this procotol. The Fe(0)/RAFT polymerization showed its superiority with low cost, eco-friendly and potential for mass production.

Reactive and functional polymers have been extensively employed in industrial applications. Glycidyl methacrylate (GMA) is an attractive monomer among them because of its economic and biological value. Homogeneous and heterogeneous GMA-based polymers have been synthesized and utilized in coating,[1] adhesives,[2] adsorbent[3] and drug-delivery,[4] and so forth. The charm of GMA comes from its easily transformable and clickable oxirane groups which can been easily opened,[5] endowing different properties to polymers. For example, they can readily react with sodium azide (NaN_3) to yield polyazidated polymers for further functionalizations *via* "click" chemistry.[6] Reaction with amines has also been used for the synthesis of hydroxylated derivatives or crosslinked structures.[7] The ring-opening of the epoxide group by thiols is an another strategy to attach pendant groups to polymer backbone.[8] In a word, numerous functional polymers have been fabricated *via* modifying GMA-based polymers. To make it suitable for advanced applications, the molecular weights (MW), molecular weight distribution (MWD) and architectures of GMA-based polymers are required to be well-defined. Thanks to the advent of control radical polymerizations (CRP), including group-transfer polymerization (GTP),[9] nitroxide-mediated polymerization (NMP),[10] atom transfer radical polymerization (ATRP)[11] and reversible addition-fragmentation chain transfer polymerization (RAFT),[12] the control over MW as well as architetures becomes more feasible and easier. However, the good control of MW and MWD of GMA polymers are usually challenging by conventional CRP, ascribing to side reactions arsing from its oxirane groups, including ring opening of oxirane group with noncomplexed ligand or other reaction additives, high polymerization temperature and inefficient initiation.[13] Herein, some improved CRP strategies are utilized, *i.e.*; initiators for continuous activator regeneration ATRP with low ATRP catalyst and ligand concentration.[13*a*] Another effective approach is to polymerize at ambient temperature or lower.[14] However, redox initiator or specific initiation source (photo, γ-ray or plasma) is usually required for low temperature polymerization, which undoubtedly cause economic or practical issues. In our previous work, we reported a successful RAFT polymerization of methyl methacrylate (MMA) under the catalysis of zero-valent iron (Fe(0)) at ambient temperature.[15(a,b)] The polymerization mechanism is supposed to be Fe(0)-mediated RAFT polymerization, wherein the RAFT agent is supposed to play a dual function; initiation and reversible chain transfer reaction to maintain the control over chain propogation. Compared with ATRP, ligand is absent in the Fe(0)-mediated RAFT polymerization. In contrast to traditional RAFT polymerization, the thermal initiator is not needed, which can induce high chain end fidelity. Therefore, Fe(0)-mediated RAFT polymerization is considered as an ideal system for the controlled polymerization of GMA with protection of oxirane group and sufficient control over MW.

In this work, Fe(0)-mediated RAFT polymerizations of GMA were undertaken at ambient temperature (25^{o}C) in DMSO with 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN) as RAFT agent, and the results were shown in Fig. 1. The reaction conditions were as follows: $[GMA]_0/[CPDN]_0/[Fe(0)]_0 = 200/(0.25,0.5,1,2)/1$, $[GMA]_0$ = 3.78 M in DMSO solution. From Fig. 1(a), it was found that the polymerizations can smoothly occur at 25^{o}C. About 85% conversion was achieved within 55 h at the molar ratio of $[GMA]_0/[CPDN]_0/[Fe(0)]_0 = 200/2/1$. Decreasing CPDN to $[GMA]_0/[CPDN]_0/[Fe(0)]_0$ = 200/1/1, 200/0.5/1, 200/0.25/1, the polymerization rate was decreased. Fig. 1(b) describes the number-average molecular weight ($M_{n,SEC}$) and molecular weight distribution (M_w/M_n) as the function of monomer conversion at various CPDN concentrations. It was found that at

$[GMA]_0/[CPDN]_0/[Fe(0)]_0 = 200/0.25/1$ or $200/0.5/1$ or $200/1/1$, the $M_{n,SEC}$ conveyed acceptable control especially at high conversion and the M_w/M_n remained narrow in most cases ($M_w/M_n < 1.35$). At low monomer conversion, the MW was much higher than the theoretical one ($M_{n,th} = ([GMA]_0/[CPDN]_0) \times M_{GMA} \times \text{conversion} + M_{CPDN}$, where M_{GMA} and M_{CPDN} represent the molecular weights of GMA and CPDN), which was ascribed to the incomplete consumption of RAFT agent at early stage of polymerization under the polymerization conditions. Whereas, under $[GMA]_0/[CPDN]_0/[Fe(0)]_0 = 200/2/1$, the MWs were poorly controlled, indicating that high CPDN concentration deteriorated the polymerization control. The reason may be due to high polymerization rate incurred by high CPDN concentration. The effects of the Fe(0) concentration on polymerization were also investigated as shown in Fig. 2. The polymerization rate ($k_p^{app} = 0.017$ h^{-1} in Figure 1) was enhanced with increasing $[GMA]_0/[CPDN]_0/[Fe(0)]_0 = 200/1/1$ to $[GMA]_0/[CPDN]_0/[Fe(0)]_0 = 200/1/2$ ($k_p^{app} = 0.023$ h^{-1}). However, the polymerization rate was slightly enhanced with $[GMA]_0/[CPDN]_0/[Fe(0)]_0 = 200/1/2$ changing to $[GMA]_0/[CPDN]_0/[Fe(0)]_0 = 200/1/4$. At $[GMA]_0/[CPDN]_0/[Fe(0)]_0 = 200/1/2$, the polymerization expressed reasonable control, while the $[GMA]_0/[CPDN]_0/[Fe(0)]_0 = 200/1/4$ produced uncontrolled MWs. These results demonstrated that high CPDN or Fe(0) concentrations was unfavourable for good controls.

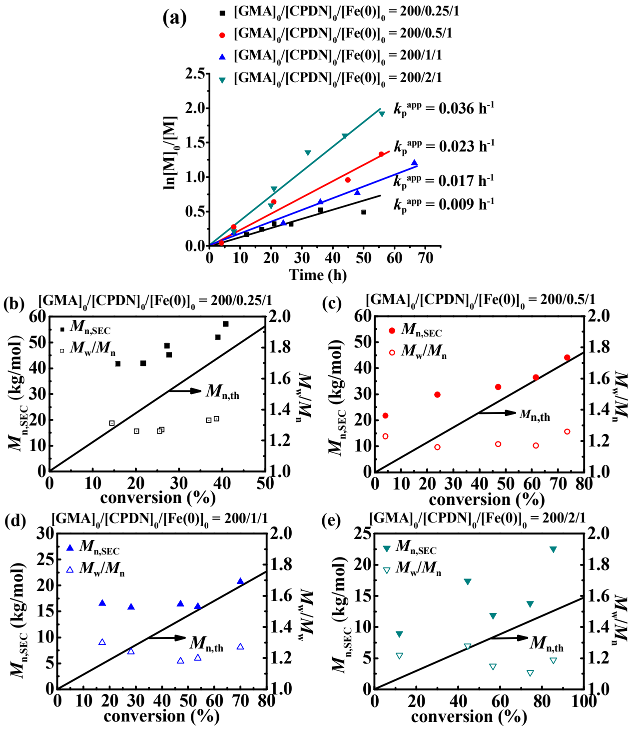


Fig. 1 Kinetic investigation (ln([M]$_0$/[M]) versus time) (a) and numberaverage molecular weight (M_n) and molecular weight distribution(M_w/M_n) (b-e) of Fe(0)/CPDN mediated polymerization of GMA at different CPDN concentration at 25 °C in DMSO.

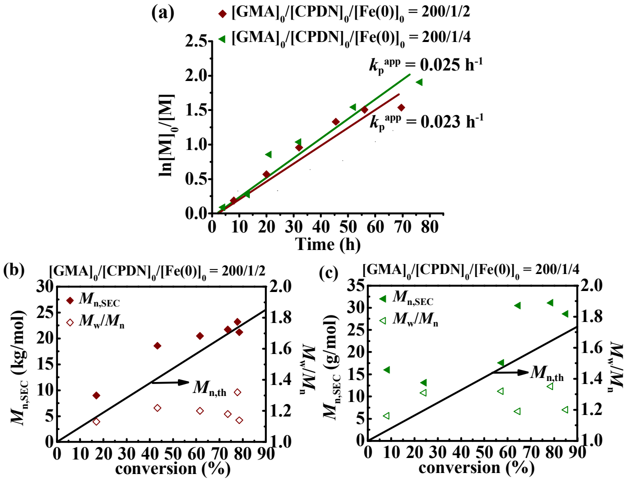


Fig. 2 Kinetic investigation (ln([M]$_0$/[M]) versus time) (a) and number average molecular weight (M_n) and molecular weight distribution(M_w/M_n) (b & c) of Fe(0)/CPDN mediated polymerization of GMA at different Fe(0) concentration at 25 °C in DMSO.

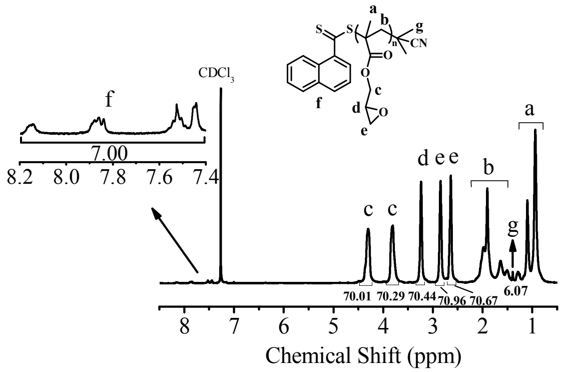


Fig. 3 ^{1}H NMR spectrum of poly(glycidyl methacrylate) (PGMA, $M_{n,SEC}$ = 9.0 kg mol^{-1}, M_w/M_n = 1.13) obtained from the Fe(0)/CPDN mediated polymerization of GMA. $CDCl_3$ was used as the solvent and tetramethylsilane (TMS) as the internal standard for NMR measurement.

Fig. 3 shows the ^{1}H NMR spectrum of the polymer ($M_{n,SEC}$ = 9.0 kg mol^{-1}, M_w/M_n = 1.13) obtained at 17.0% conversion from the polymerization with 200/1/2 of $[GMA]_0/[CPDN]_0/[Fe(0)]_0$ in Fig. 2. The chemical shifts at 4.31 ppm and 3.81 ppm (c, 2H, $I_{4.31} = 68.01$, $I_{3.81} = 68.29$) could be assigned to the protons of methylene from GMA. The signals at $\delta = 3.24$ ppm (d, 1H, $I_{3.24} = 68.44$) and $\delta = 2.84$ ppm and 2.63 ppm (e, 2H, $I_{2.84} = 68.96$, $I_{2.63} = 68.67$) was assigned to the protons of the oxirane ring. The integral value ratio of d and e was approximately equal to 1:2, and the absence of any other undesired peaks in the ^{1}H NMR spectrum revealed that the epoxy group remained intact after polymerization. The peaks at $\delta = 7.40 \sim 8.20$ ppm (f, 7H, $I_{7.40\text{-}8.20} = 7.00$) corresponded to the aromatic protons of the CPDN units indicating that the obtained polymers (ω chain end) contained the moiety of CPDN. The peak at $\delta = 1.40$ ppm (g, 6H, $I_{1.40} = 6.07$) was assigned to methyl from CPDN at polymer α chain end. The molecular weight ($M_{n,NMR}$) of PGMA can be calculated from the integrals in ^{1}H NMR ($M_{n,NMR} = (I_{7.40\text{-}8.20}/7) \times M_{GMA} \times I_{4.31} + M_{CPDN}$). The molecular weight of PGMA sample calculated from the ^{1}H NMR spectrum ($M_{n,NMR}$) was 9.9 kg mol^{-1}, which was in reasonable agreement with M_n determined by SEC. The percentage of chain-end functionality (f) of the polymer products was determined by ^{1}H NMR by comparing the integrals of δ = 7.40 ~ 8.20 ppm (7H, $I_{7.40\text{-}8.20}$), corresponding to the protons of naphthalene group, and δ = 1.40 (6H, $I_{1.40}$) arising from the protons at the α-position of isobutyronitrile chain end ($f = (I_{7.40\text{-}8.20}/7)/(I_{1.40}/6)$). f was approximately 98.8%, indicating that most of GMA polymer chains were "living".[16]

An additional investigation was conducted to verify the chain end functionality of the PGMA. Herein, PGMA of $M_{n,SEC}$ = 16.4 kg mol^{-1}, M_w/M_n = 1.18 obtained from the Fe(0)/CPDN mediated polymerization ([GMA]$_0$/[CPDN]$_0$/[Fe(0)]$_0$ = 200/1/1) was used as a macro-RAFT agent/mediator for a chain extension reaction. The reaction was carried out for 45 h in DMSO at 25 °C using Fe(0) as catalyst at molar ratio [GMA]$_0$/[PGMA]$_0$/[Fe(0)]$_0$ = 500/1/1. The obtained polymer ($M_{n,SEC}$ = 60.7 kg mol^{-1}) had a narrow MWD (M_w/M_n = 1.16). As shown in Fig. 4(a), most of the end groups of the polymer participate in chain extension reaction, further proving that the polymer end groups were reactivable. Chain extension with MMA was also implemented. The results showed that the chain extension of MMA by using PGMA as macro-mediator was successful. The MW shifted from 21.4 kg/mol to 42.1 kg/mol as shown in Fig. 4(b).

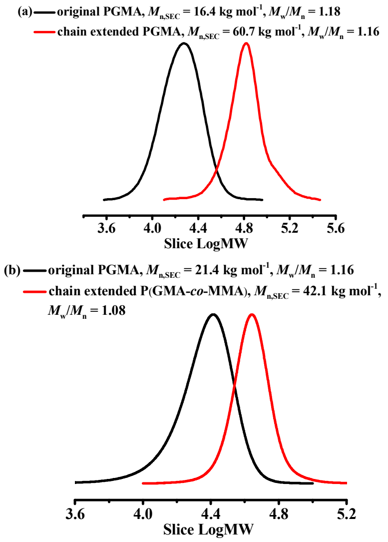


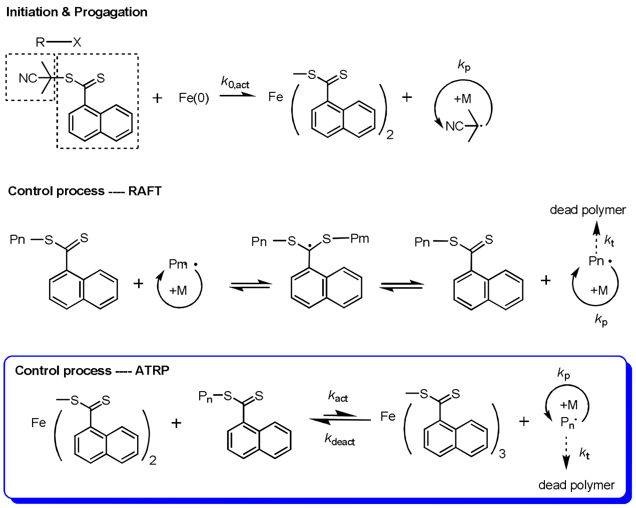
Fig. 4 Chain extension of poly(glycidyl methacrylate) (PGMA) macroinitiator with GMA (a) and MMA (b). Experimental conditions: (a) [GMA]$_0$/[PGMA]$_0$/[Fe(0)]$_0$ = 500/1/1, [GMA]$_0$ = 2.52 M in DMSO at 25 °C; (b) [MMA]$_0$/[PGMA]$_0$/[Fe(0)]$_0$ = 500/1/1, [MMA]$_0$ = 4.71 M in DMSO at 25 °C.

For verifying the universality of Fe(0)/RAFT mediated polymerization, many tentative experiments were conducted, and the results are summarized in Table 1. It can be seen that the polymerizations were controlled in polar solvent (DMF or DMSO), while in anisole, toluene or dioxane (items 1-5), the polymerization cannot happen. The results complied with the previous report and the mechanism has been discussed.[15a] Using Fe(0) wire instead of Fe(0) power, the polymerizations also showed good control evidence, implying that the catalyst can be recycled easily with good prospects for large scale production. However, the combination of Cu(0) powder with CPDN, the polymerization of GMA was out of control with very high MW (item 6). Some other transition metals, such as Co(0), Ni(0), and Zn(0) instead of Fe(0), good control polymerization behavior of GMA was also observed (items 7-9). Comparable results of the polymerizations of MMA by these zero-valent metals were also found (items 10-13) (kinetic investigation of Co(0)/CPDN mediated polymerization was also carried out under different conditions, see Fig. S1 & S2). Some other functional monomers, 4-vinylpyridine (4VP) and butyl methacrylate (BMA) were testified, the polymerizations also showed controllable behaviour by Fe(0)/CPDN mediated polymerization (items 14 & 15). Interestingly, the combination of Fe(0) with hydrophilic RAFT agent (4-(4-cyanopentanoicacid) dithiobenzoate (CPADB) catalyst system can also enable good control polymerization of hydrophilic monomers in aqueous solution, such as 2-(dimethylamino)ethyl methacrylate (DMAEMA) or poly(ethylene glycol) monomethyl ether methacrylate (PEGMA).

Table. 1 Fe(0)/RAFT mediated Polymerizations under Various Conditions[a]

item	contents	Temperature (°C)	time (h)	Conv. (%)	$M_{n,SEC}$ (kg mol^{-1})	M_w/M_n	$M_{n,th}$ (kg mol^{-1})
1	GMA/CPDN/Fe(0)/anisole	25	30	0	--	--	--
2	GMA/CPDN/Fe(0)/dioxane	25	30	1.4	--	--	--
3	GMA/CPDN/Fe(0)/toluene	25	30	8.1	--	--	--
4	GMA/CPDN/Fe(0)/DMF	25	30	35.4	15.4	1.20	10.3
5	GMA/CPDN/Fe(0) wire/DMSO	25	30	13.3	13.4	1.18	4.1
6	GMA/CPDN/Cu(0)/PMDETA/DMSO	25	56	high	uncontrolled	--	--
7	GMA/CPDN/Co(0)/ DMSO	25	48	81.2	23.3	1.16	23.4
8	GMA/CPDN/Ni(0)/ DMSO	25	48	75.7	22.3	1.15	21.8
9	GMA/CPDN/Zn(0)/ DMSO	25	72	54.0	21.6	1.20	15.6
10	MMA/CPDN/Co(0)/DMSO	25	40	94.0	22.1	1.16	19.1
11	MMA/CPDN/Ni(0)/DMSO	25	75	81.4	20.0	1.21	16.6
12	MMA/CPDN/Mn(0)/DMSO	25	75	21.2	10.9	1.21	4.5
13	MMA/CPDN/Zn(0)/DMSO	25	48	58.2	15.3	1.19	11.9
14	4VP/CPDN/Fe(0)/DMF	60	100	35.5	12.1	1.08	7.7
15	BMA/CPDN/Fe(0)/DMSO	25	72	25.3	12.1	1.20	7.5
16	DMAEMA/CPADB/Fe(0)/water	70	40	27.2	2.9	1.17	8.8
17	PEGMA(300)/CPADB/Fe(0)/water	70	72	45.7	17.3	1.28	13.9

[a] 1, 2 ,3 and 4: $[GMA]_0/[CPDN]_0/[Fe(0)]_0 = 200/1/1$, $[GMA]_0 = 3.78$ M in different solutions; 5: $[GMA]_0/[CPDN]_0 = 200/1$, $[GMA]_0 = 3.78$ M, Fe(0) Wire = 1 cm, diameter = 1 mm; 6: $[GMA]_0/[CPDN]_0/[Cu(0)]_0/[PMDETA]_0 = 200/1/1/1$, $[GMA]_0 = 3.78$ M; 7, 8 and 9: $[GMA]_0/[CPDN]_0/[\ Metal]_0 = 200/1/1$, $[GMA]_0 = 3.78$ M; 10, 11, 12 and 13: $[MMA]_0/[CPDN]_0/[Metal]_0 = 200/1/1$, $[MMA]_0 = 4.71$ M; 14: $[4VP]_0/[CPDN]_0/[Fe(0)]_0 = 200/1/1$, $[4VP]_0 = 4.70$ M; 15: $[BMA]_0/[CPDN]_0/[Fe(0)]_0 = 200/1/1$, $[BMA]_0 = 3.15$ M; 16: $[DMAEMA]_0/[CPADB]_0/[Fe(0)]_0 = 200/1/1$, $[DMAEMA]_0 = 2.97$ M; 17: $[PEGMA(300)]_0/[CPADB]_0/[Fe(0)]_0 = 100/1/1$, $[PEGMA(300)]_0 = 1.85$ M.



Scheme 1. Proposed hybrid mechanism for GMA polymerization with CPDN and Fe(0).

On the basis of our work, a hybrid polymerization mechanism (RAFT&ATRP) is proposed in Scheme 1. In the initial stage, Fe(0) serves as an activator that cleaves the C-S bond of the RAFT agent to generate initiating radicals, which then launch the polymerization in a classical RAFT process with the unreacted RAFT agent. The formed Fe(II) and Fe(III) act as activator and deactivator, forming an equilibrium between dormant and active species *via* an ATRP-like mechanism.[15*c*,17] However, from the polymerization kinetics in Figure 1, the ATRP mechanism was supposed to dominate control process.[15*c*,17]

In this work, the Fe(0)/CPDN catalyst system was successfully utlized for the GMA polymerization at 25 °C. Good livingness of the polymerization was observed with appropriate Fe(0) and CPDN concentrations. Other functional monomers and hydrophilic monomers are also applicable by this strategy. This Fe(0)/CPDN catalyst system provided an effective, alternative and facile approach for controlled polymerization, especially for those monomers with subtle groups.

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Notes and references

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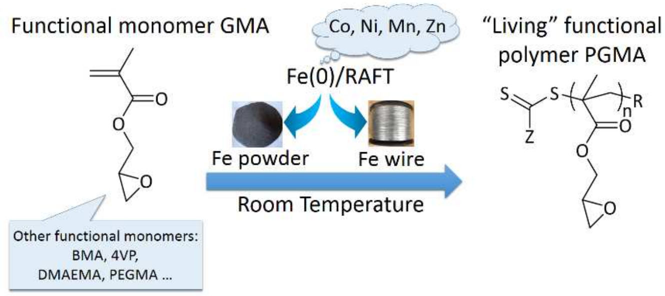

Zero Valent Metal/RAFT Agent Mediated CRP of Functional Monomers at Room Temperature: a Promising Catalyst System for CRP

Yuwei Gu, Junfei Zhao, Qingqing Liu, Xiangqiang Pan, Wei Zhang, Zhengbiao Zhang*, and Xiulin Zhu*

A facile approach to synthesize GMA polymers using Fe(0)/RAFT agent mediated control radical polymerization.