

Supplemental Information

Influence of Less Active Initiator on the Living Performance of Atom Transfer Radical Polymerization and the Structure of Grafted Copolymer Synthesized

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Materials

Ascorbic acid (VC), D-(+)-glucose and tin (II) 2-ethylhexanoate (Sn(Oct)₂) were purchased from Aladdin Reagent Co. (Shanghai, China) with the highest purity and used as received without further purification. Inorganic sulfites (Na₂S₂O₃•5H₂O, Na₂S₂O₄ and Na₂SO₃) were obtained from Yong Sheng Fine Chemical Co. (Tianjin, China). Metallic Zinc (Zn), Iron (Fe), and Magnesium (Mg) were purchased from Kermel Chemical Co. (Tianjin, China) and used as received.

Result and Discussion

FTIR and DSC Characterization of P(VDF-CTFE)-g-PMMA Copolymer

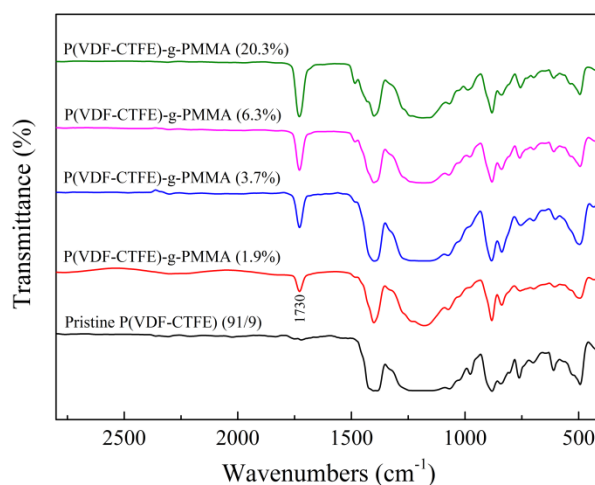


Fig. 1S FTIR spectra of pristine P(VDF-CTFE) and P(VDF-CTFE)-g-PMMA with different PMMA contents.

The grafting of MMA onto P(VDF-CTFE) could be identified on FTIR spectroscopy as shown in Fig. 1S. The characteristic peak at 1730 cm⁻¹ corresponding to the ester group of MMA was observed in the resultant copolymer, which clearly confirms the presence of PMMA segments. As the content of PMMA increases, the intensity of this peak is remarkably enhanced.

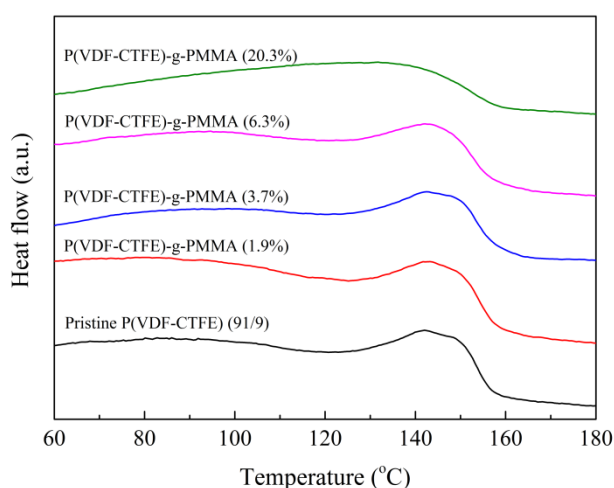


Fig. 2S DSC thermograms of pristine P(VDF-CTFE) and P(VDF-CTFE)-g-PMMA graft copolymers with varied PMMA contents obtained from the second heating circle at a heating rate of 10°C/min.

Thermal property of P(VDF-CTFE)-g-PMMA was characterized with DSC analysis at a heating rate of 10°C min⁻¹ as shown in Fig. 2S. Only one endothermic peak was observed on each curve below 180°C attributed to the melting of the P(VDF-CTFE) crystalline phase of the copolymers. The melting temperature shifting from about 145 to 130°C and the melting enthalpy decreasing from 5.67 to 0.42 J/g with the increase of PMMA segments indicate the crystallinity reduction of P(VDF-CTFE)-g-PMMA as a function of PMMA content.

Synthesis of P(VDF-CTFE)-g-PMMA catalyzed with FeCl₂/PPh₃ without reducing agent

Table 1S Synthesis of P(VDF-CTFE)-g-PMMA catalyzed with FeCl₂/PPh₃ without any reducing agent under varied reaction conditions.

Entry ^a	[I] ₀ /[Cat] ₀ /[L] ₀ ^b (mol%)	Temperature (°C)	Time (h)	MMA grafted ^c (%)
1	1 : 1 : 2	100	1	0.32
2	1 : 1 : 2	100	2	0.49
3	1 : 1 : 2	100	4	0.57
4	1 : 1 : 2	100	8	0.60
5	1 : 1 : 2	100	24	0.62
6	1 : 1 : 2	90	24	0
7	1 : 1 : 2	105	24	0
8	1 : 1.5 : 3	100	24	1.10
9	1 : 2 : 4	100	24	0.72

^a 1 g P(VDF-CTFE) (VDF/CTFE = 91/9 in mol%) and 30 mL DMSO are utilized as initiator and solvent, respectively. The initial molar ratio of initiator to monomer is fixed to 1 : 28.7 in all the entries.

^b [I]₀/[Cat]₀/[L]₀ is the initial molar ratio of catalyst to initiator to ligand.

^c The MMA grafted is referring to the percentage of the PMMA grafted onto P(VDF-CTFE), which is calculated from eq (2).

Synthesis of P(VDF-CTFE)-*g*-PMMA catalyzed with FeCl₂/PPh₃ with different kinds of reducing agent

As suggested by Y. Z. Zhang and his co-workers,^[1] metallic Mg, Zn and Fe were investigated as reducing agents in present work. P(VDF-CTFE)-*g*-PMMA copolymers were synthesized using the initial molar ratio of reagents [R-Cl] : [FeCl₂] : [PPh₃] : [RA] = 1 : 1 : 2 : 1, in DMSO at 100°C. After removing homo-PMMA from the resultant copolymer, the MMA conversion and the composition of P(VDF-CTFE)-*g*-PMMA was calculated from eq (1-3) and listed in Table 1S. As shown in entries 1-3 of Table 1S, the introduction of reducing agent leads to an increasing MMA conversion from 0.62% (entry 5 in Table 1S) to 0.78%, 2.53%, and 7.18%. After PMMA homopolymer was removed, the molar number of grafted PMMA was improved to 2.0, 6.5, and 18.6 in every 100 main chain units (the total amount of VDF and CTFE units) with Mg, Zn and Fe using as reducing agents, respectively. Apparently, adding reducing agents could effectively improve MMA conversion as well as the molar content of MMA grafted onto P(VDF-CTFE). However, -CF=CH- signals were obtained at about 6.3 ppm in the ¹H NMR spectra (Fig. 3S) of grafted copolymers prepared using these metals as reducing agent. Our previous study^[2] has clearly demonstrated that the elimination reaction is mostly taking place in the dehydrochlorination mechanism catalyzed with basic compounds (reductive metals Mg, Zn and Fe in this case). Therefore, these reductive metals are not desirable reducing agents for the synthesis of P(VDF-CTFE)-*g*-PMMA by ATRP.

Table 2S Influence of reducing agent on the grafting polymerization of MMA onto P(VDF-CTFE).

Entry ^a	RA	MMA conversion ^b (%)	MMA grafted (%)	VDF/CTFE/MMA ^c (in molar)
1	Mg	1.73	0.78	91/9/2.0
2	Zn	3.44	2.53	91/9/6.5
3	Fe	8.68	7.18	91/9/18.6

4	Na ₂ S ₂ O ₄	15.66	2.01	91/9/5.2
5	Na ₂ SO ₃	38.99	3.12	91/9/8.1
6	Na ₂ S ₂ O ₃ •5H ₂ O	43.24	4.32	91/9/11.2
7	Sn(Oct) ₂	6.58	3.48	91/9/9.0
8	D-(+)-glucose	9.94	4.64	91/9/12.0
9	VC	20.25	16.29	91/9/42.1

^a The initial molar ratio of [I]₀/[Cat]₀/[L]₀/[RA]₀/[M]₀ is fixed to 1 : 1 : 2 : 1 : 28.7 in all the entries. The reaction is conducted in 30 mL DMSO at 100°C for 24 h with 1 g P(VDF-CTFE) as initiator.

^b MMA conversion is calculated from eq (1), referring to the overall MMA polymerized.

^c The molar ratio of VDF, CTFE and MMA units is estimated from eq (3).

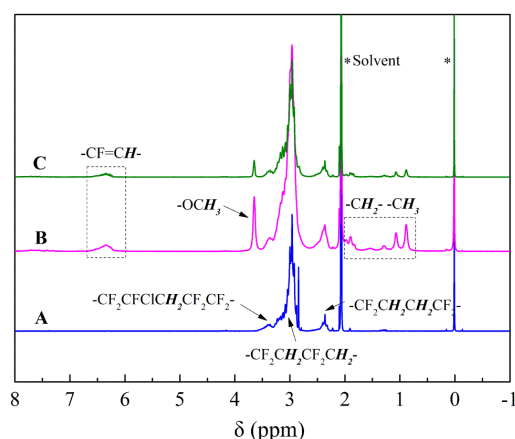
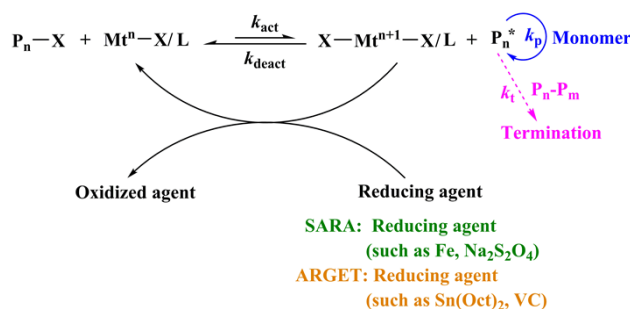


Fig. 3S ¹H NMR spectra of (A) pristine P(VDF-CTFE), (B) P(VDF-CTFE)-g-PMMA containing homo-PMMA and (C) P(VDF-CTFE)-g-PMMA after homo-PMMA was removed using Mg as reducing agent.

C. M. R. Abreu and his co-workers^[3] reported the use of inexpensive and commonly used inorganic sulfites such as sodium dithionite (Na₂S₂O₄), sodium metabisulfite (Na₂S₂O₅), and sodium bisulfite (NaHSO₃) as reducing agents for ATRP, following the SARA (supplemental activator and reducing agent) ATRP mechanism (Scheme 1S). In combination with CuBr₂/Me₆TREN, they produced poly(methyl

acrylate) with controlled molecular weight, low dispersity ($M_w/M_n = 1.05$), and well-defined chain-end functionality. Therefore, inorganic sulfites Na_2SO_3 , $\text{Na}_2\text{S}_2\text{O}_4$ and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ were employed as reducing agents in this work as well under the consistent other reaction conditions as used above. As shown in entries 4-6 of Table 2S, the conversion of MMA is significantly increased to 15.66%, 38.99%, and 43.24% when Na_2SO_3 , $\text{Na}_2\text{S}_2\text{O}_4$ and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ were added in equal molar amounts of FeCl_2 . But only about one tenth of these MMA monomers was grafted onto P(VDF-CTFE) and most of them were homopolymerized. The homopolymerization of MMA initiated with potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) and ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) may explain the formation of PMMA homopolymer in large quantity during the synthesis of P(VDF-CTFE)-*g*-PMMA copolymers using these inorganic sulfites as reducing agents. Obviously, these inorganic sulfites were not useful reducing agents for the synthesis of P(VDF-CTFE)-*g*-PMMA either, although they might be good ones for the synthesis of homo-PMMA initiated with small molecular initiators.



Scheme 1S General mechanism of SARA ATRP and ARGET ATRP.

Vitamin C (VC), D-(+)-glucose and tin (II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) have been extensively adopted as reducing agents in the ARGET-ATRP (Scheme S1) as well because of their high solubility in organic solvents.^[4,5] In order to improve the grafting amount of MMA rather than raising the homopolymerization of MMA, $\text{Sn}(\text{Oct})_2$, glucose and VC were used as reducing agents in present work. As shown in entries 7-9 of Table 2S, the molar number of MMA grafted is significantly increased to 9.0, 12.0 and 42.1 in every 100 main chain units respectively when $\text{Sn}(\text{Oct})_2$, D-(+)-glucose, and VC in equimolar amounts of FeCl_2 were added. VC as reducing

agent shows the highest MMA conversion and very low content of homo-PMMA. That means VC is the most desirable reducing agent for the grafting reaction of P(VDF-CTFE)-*g*-PMMA and is used in all the following copolymerization in FeCl₂/PPh₃ systems.

References

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