Electronic Supplementary Information

Activation of Different C-F Bond in Fluoropolymers for Cu(0) Mediated Single Electron Transfer Radical Polymerization

Biyun Peng,[†] Jian Wang,[†] Meng Li,[‡] Miao Wang,[†] Shaobo Tan,[,†] and Zhicheng Zhang*[,†]*

[†]Xi'an Key Laboratory of Sustainable Energy Materials Chemistry, School of Chemistry, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, P. R. China

[‡]School of Materials Science and Chemical Engineering, Xi'an Technological University, Xi'an 710032, Shaanxi, P. R. China

E-mail: shaobotan.1987@xjtu.edu.cn (T.S.)

E-mail: zhichengzhang@mail.xjtu.edu.cn (Z.Z.)

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1. DSC data

The crystalline properties of the graft copolymer were obtained from DSC thermograms, as shown in **Figure S1** and **Table S1**. Obviously, with the increase of grafted content, the crystallinity is decreased from 18.4% (c-P(VDF-TrFE)) to 5.0% (c-(P(VDF-TrFE)-*g*-PMMA, 20.7 wt%) (**Table S1**). For c-P(VDF-TrFE), the endothermic peaks located at 149 °C and 130 °C are corresponding to the ferro-to-paraelectric transition temperature (T_C) and melting point (T_m), respectively.

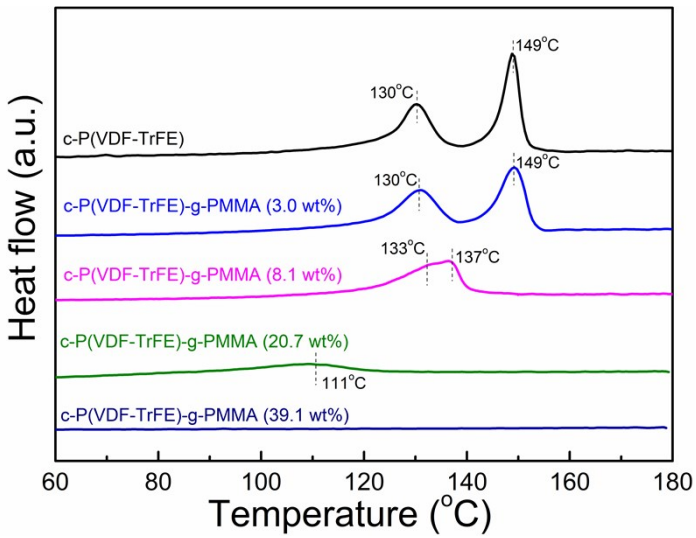

Figure S1. Second-heating DSC thermograms of c-P(VDF-TrFE) (80/20 mol%) and the graft copolymers with varying PMMA contents.

Table S1 The melting temperature and F-P transition temperature of the copolymers.

Sample	ΔH_f/J·g^{-1}	T_C/ °C	T_m/ °C	χ_c/%*
c-P(VDF-TrFE) (80/20 mol%)	18.9	130	149	18.4

c-P(VDF-TrFE)-*g*-PMMA (3.0 wt%)	18.8	130	149	18.3
c-P(VDF-TrFE)-*g*-PMMA (8.1 wt %)	9.1	133	137	8.9
c-P(VDF-TrFE)-*g*-PMMA (20.7 wt %)	5.2	/	111	5.0
c-P(VDF-TrFE)-*g*-PMMA (39.1 wt %)	/	/	/	/

*The crystallinity is calculated from $\chi_c=\Delta H_f/\Delta H_f^*\times 100\%$, where the value of ΔH_f^* is 102.5 $J\cdot g^{-1}$ corresponding to the melting enthalpy of PVDF with 100% crystallinity.

2. GPC traces

GPC measurements show that the initial negative refractive index signal (relative to solvent) of the macro-initiator becomes a positive one (**Figure S2**), and a single peak is observed in all the graft copolymers indicating the successful graft polymerization.

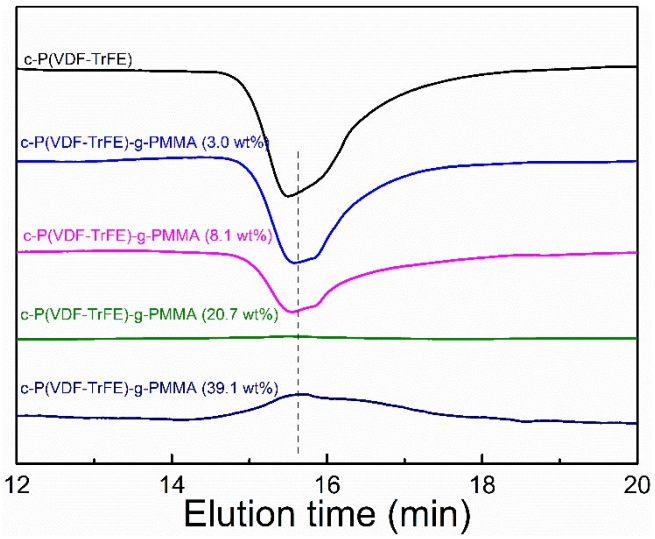

Figure S2. GPC traces of c-P(VDF-TrFE) and the graft copolymers with varying PMMA contents.

3. Influence of reaction conditions on the graft polymerization from c-P(VDF-TrFE)

A series of c-P(VDF-TrFE)-*g*-PMMA graft copolymers were synthesized *via* SET-CRP process under different reaction conditions, as presented in **Table S2**. The effects of different factors on the graft polymerization were investigated, including solvent, temperature, catalyst (Cu^0/Bpy) and monomer dosage. Firstly, under the same reaction conditions, the efficiency of graft polymerization in DMSO (entry 1) is higher than that in NMP (entry 2) and DMF (entry 3). By calculating, the grafted amount of PMMA in the graft copolymer conducted in DMSO is 39.1 wt%, while its value is only 6.7 and 2.5 wt% in DMF and NMP, respectively. This may be because the disproportionation reaction of Cu^IF/Bpy_2 in DMSO is faster than that in NMP and DMF, thus activating more C-F bonds with a higher rate. Next, in order to study whether the polymerization is sensitive to temperature changes, the graft polymerization was carried out at 80-100 ^oC (entry 1, 4 and 5). When the reaction was conducted at low temperature (80 ^oC), the grafted PMMA content is decreased from 39.1 to 4.8 wt%. However, when the temperature is increased to more than 100 ^oC, gelation (cross-linking) occurs in a short time, so the optimal temperature is 100 ^oC. Finally, the influence of $[TrFE]_0/[Cu^0]/[Bpy]$ in molar ratio (entry 1 and 6) and monomer dosage (entry 7) on the graft polymerization were investigated under the same conditions. Obviously, the higher the catalyst and monomer content, the higher the grafted PMMA content. When molar ratio of $[TrFE]_0/[Cu^0]/[Bpy]$ is fixed at 3:1:2, the grafted content reaches the highest value (39.1

wt%). As discussed above, the reaction conditions for the graft polymerization should be optimized to avoid some side reactions like cross-linking.

Table S2. Graft polymerization from c-P(VDF-TrFE) under varied reaction conditions.

Entry[a)]	$[TrFE]_0/[Cu^0]/[Bpy]$	Solvent	MMA/mL	T/°C	MMA grafted[b)] /mol%	PMMA content[c)] /wt%
1	3/1/2	DMSO	8	100	17.0	39.1
2	3/1/2	NMP	8	100	0.7	2.5
3	3/1/2	DMF	8	100	1.9	6.7
4	3/1/2	DMSO	8	90	1.6	5.6
5	3/1/2	DMSO	8	80	1.3	4.8
6	3/0.5/1	DMSO	8	100	6.6	19.8
7[d)]	3/1/2	DMSO	4	100	7.4	12.2

[a)]The polymerization reaction was conducted using 2.0 g of c-P(VDF-TrFE) as the initiator in 120 mL solvent for 12 h; [b)]MMA grafted (mol%) was calculated with equation (2); [c)]PMMA content was the weight percentage of PMMA in the graft copolymer. [d)]Adding 4 mL MMA.

4. The composition of graft copolymers initiated with different PVDF-based fluoropolymers at different reaction times.

In addition, taking the graft polymerization reaction for 9 h as an example, we compared the topological structure of graft copolymers initiated with different PVDF-based fluoropolymers, and the results were listed in **Table S3**. The c-P(VDF-TrFE) exhibits the highest grafted content of 12.83 and the lowest average chain length (4.56), namely, every grafted PMMA side chains contains about 4.56 MMA units.

Table S3 The composition of graft copolymers initiated with different PVDF-based fluoropolymers at different reaction times.

Entry	Time /h	$[R\text{-}F]_i$ /mmol	PMMA grafted[a)] /mmol	Average chain length	$[R\text{-}F]_i$ /%
c-P(VDF-TrFE)-*g*-PMMA	0	0	0	/	0
	2	0.39	0.62	1.57	6.65
	3	0.64	1.77	2.76	10.85
	6	2.04	5.24	2.57	34.40
	9	2.81	12.83	4.56	47.45
	12	3.50	12.92	3.70	59.05
h-P(VDF-TrFE)-*g*-PMMA	0	0	0	/	0
	2	0	0	/	0
	3	0.20	0.41	2.08	3.30
	6	0.34	1.74	5.12	5.75

	9	0.46	5.85	12.75	7.75
	12	0.47	6.50	13.72	8.00

[a)]PMMA grafted refers to the molar content of grafted PMMA in the graft copolymer.

5. NMR spectra of c-P(VDF-TrFE) and c-P(VDF-TrFE)-*g*-PMMA.

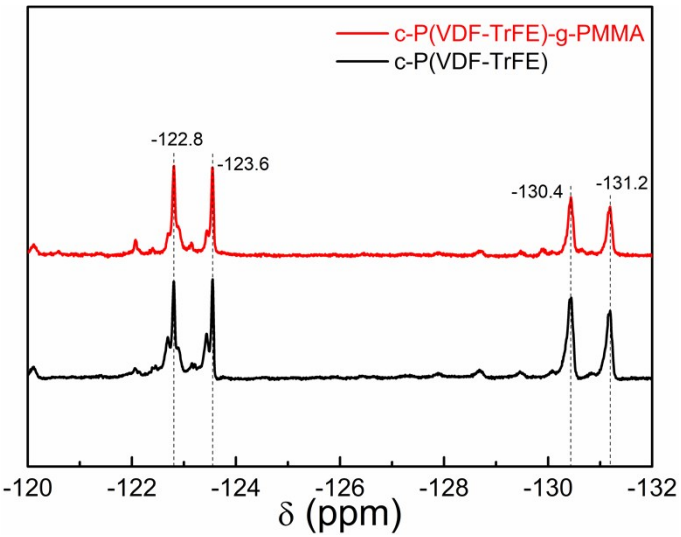

Figure S3. The partial ^{19}F NMR spectra from -120 to -132 ppm.

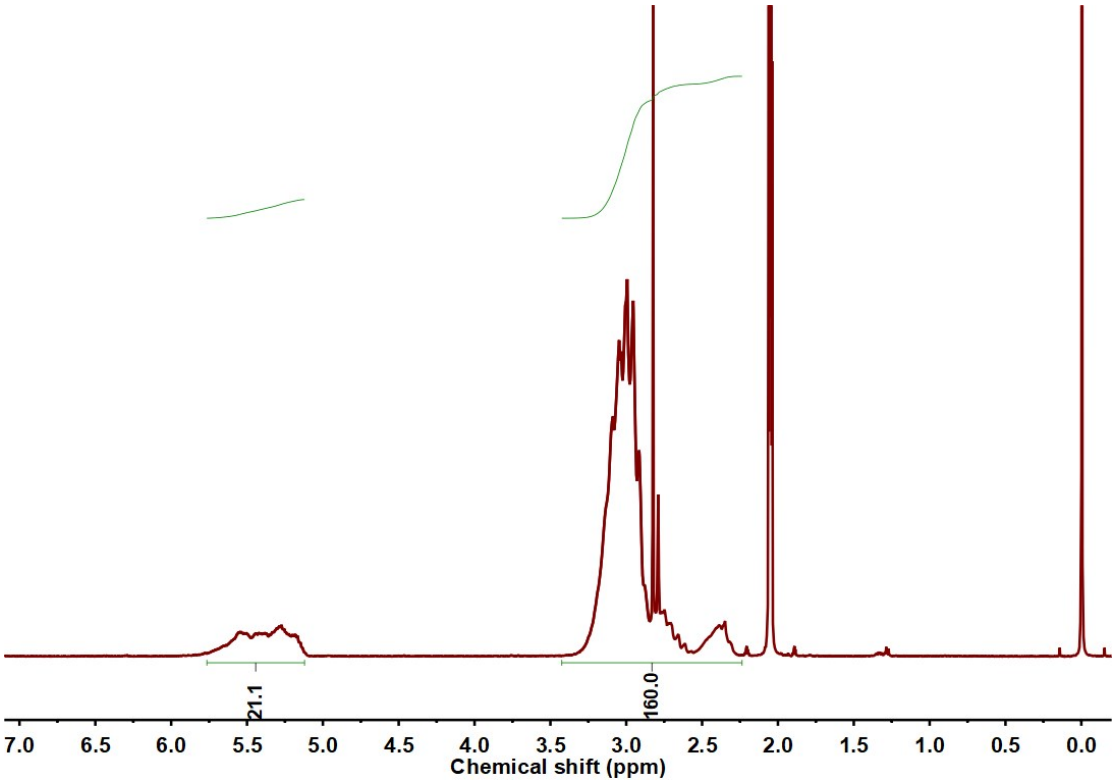

Figure S4. ^{1}H NMR spectrum of c-P(VDF-TrFE).

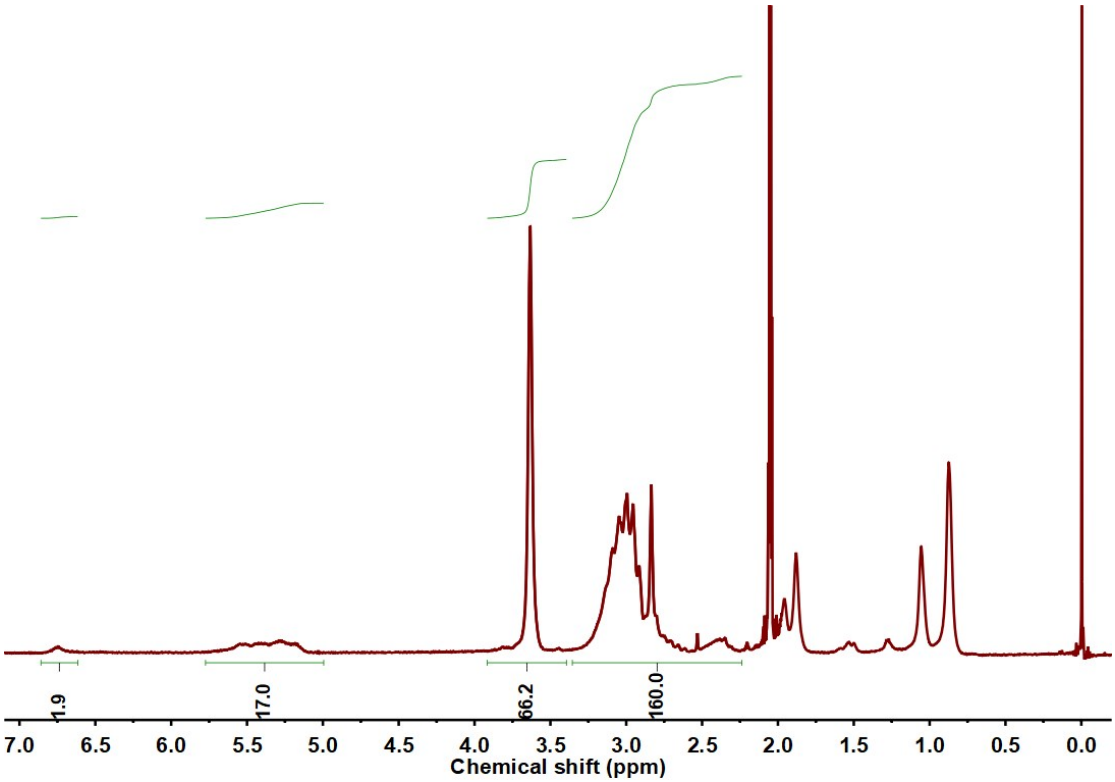

Figure S5. ^{1}H NMR spectrum of c-P(VDF-TrFE)-*g*-PMMA.

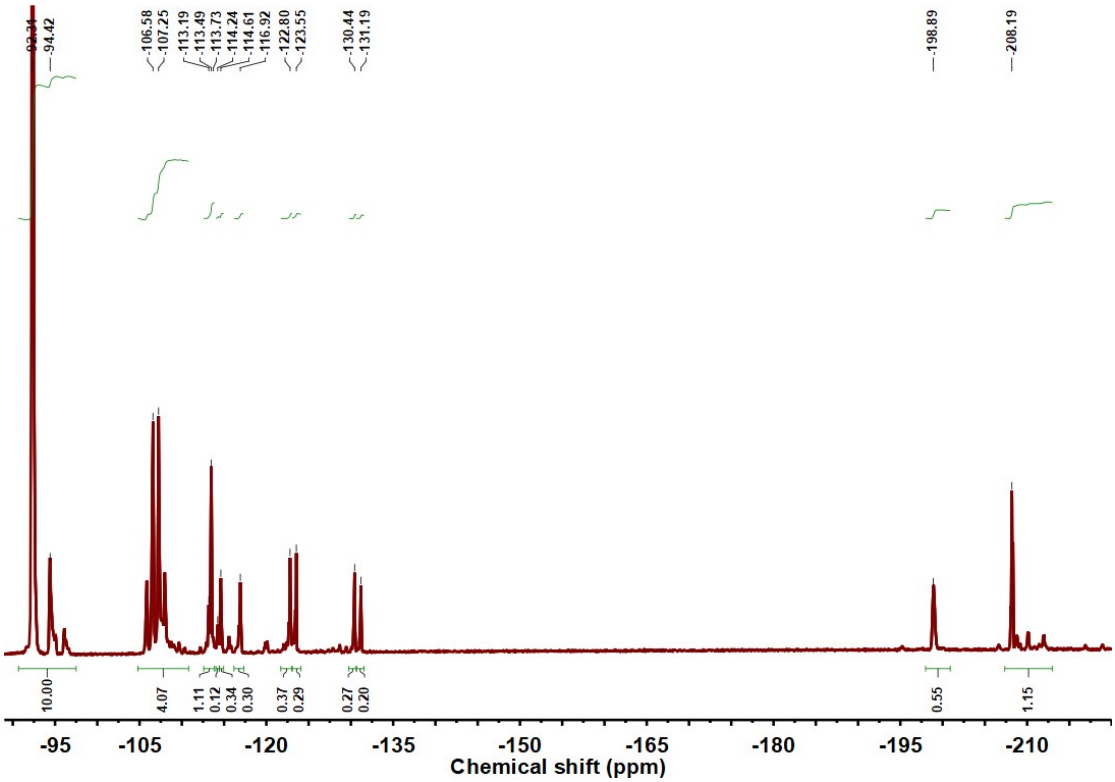

Figure S6. ^{19}F NMR spectrum of c-P(VDF-TrFE).

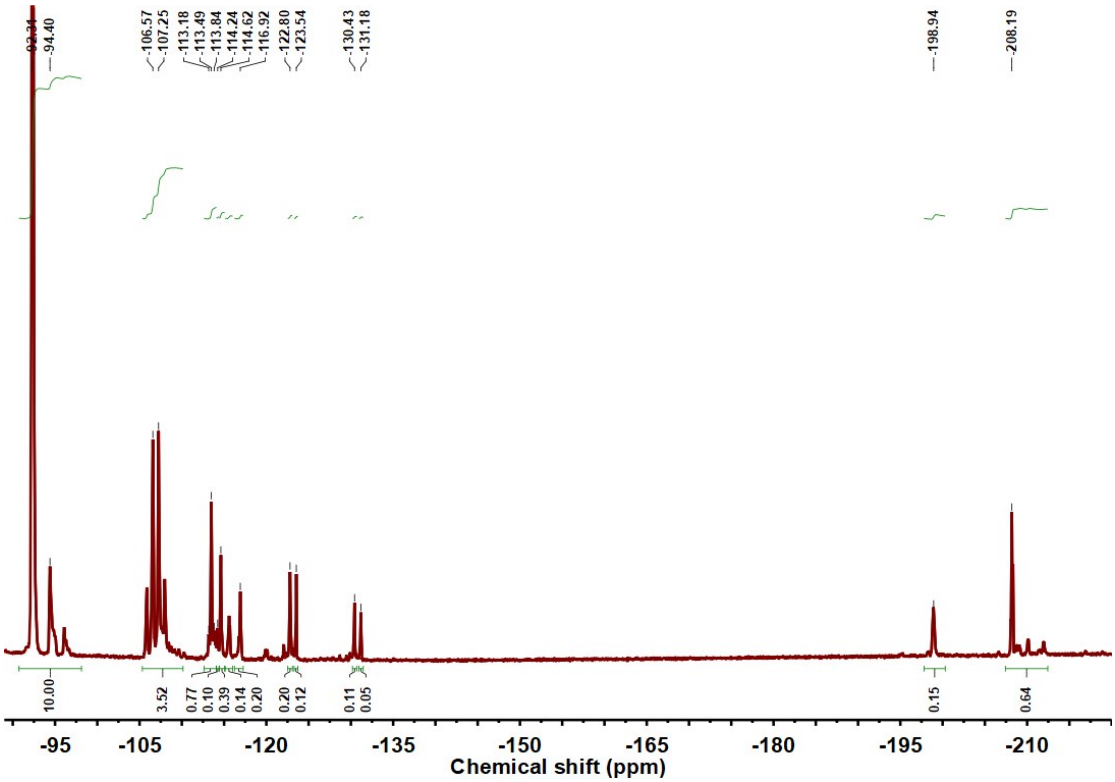

Figure S7. ^{19}F NMR spectrum of c-P(VDF-TrFE)-*g*-PMMA.