Supporting information

Synthesis and Characterization of Thermally Self-curable Fluoropolymer Triggered by TEMPO in One-pot for High Performance Rubber Application

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1. Synthesis and characterization of thermally self-curable fluoropolymer.

A series of resultant copolymers from P(VDF-*co*-CTFE) have been synthesized under alternated reaction conditions including reaction temperature, reaction time, ligand, dosage of TEMPO, solvents and copper complex as listed in Table 1S.

Table 1S. Reaction conditions for the synthesis of thermally self-curable copolymers.[a]

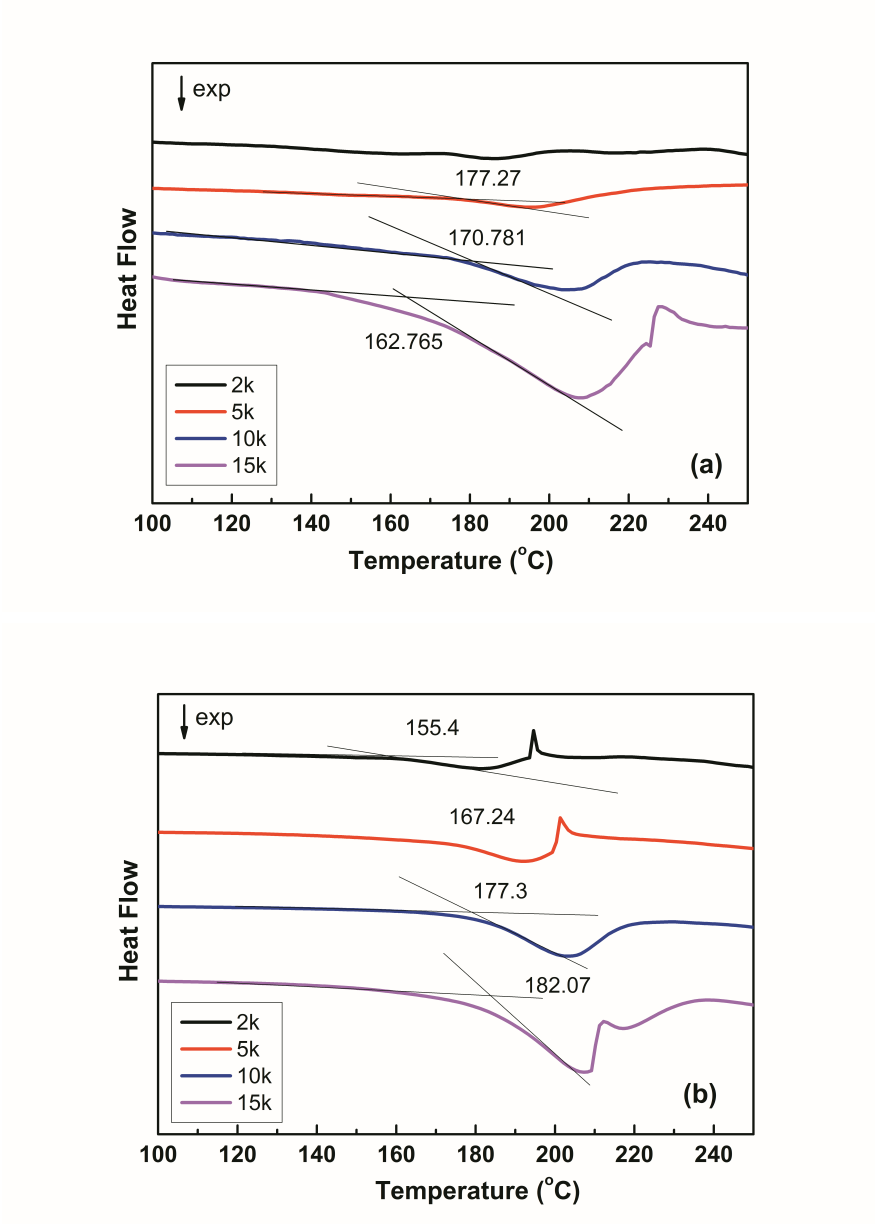
Entry	CuX/Cu mmol	Ligand mmol	Solvent mL	TEMPO mmol	Temp °C	Time h	Grafted TEMPO mol%	Double bond mol%	Limiting viscosity[b] (ml/g)
1	CuCl/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	26.8	80	0.5	0.90	5.53	
2	CuCl/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	26.8	80	2	3.21	7.51	
3	CuCl/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	26.8	80	4	4.76	7.51	
4	CuCl/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	26.8	80	6	6.14	7.85	
5	CuCl/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	26.8	80	8	6.91	8.00	
6	CuBr/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	26.8	80	0.5	0.86	3.95	
7	CuBr/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	26.8	80	2	3.71	6.57	

8	CuBr/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	26.8	80	4	5.50	6.79	
9	CuBr/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	26.8	80	6	6.72	7.68	
10	CuBr/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	26.8	80	8	7.54	8.04	
11	CuCl/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	26.8	100	0.5	2.94	5.62	
12	CuCl/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	26.8	100	1	5.58	6.57	
13	CuCl/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	26.8	100	2	7.59	8.05	
14	CuCl/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	26.8	100	4	8.34	9.27	
15	CuCl/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	26.8	100	6	8.62	10.92	
16	CuCl/Cu(2.68/5.36)	BPy(5.36)	DMF(40)	26.8	80	0.5	1.92	6.12	
17	CuCl/Cu(2.68/5.36)	BPy(5.36)	DMF(40)	26.8	80	1	3.70	5.88	
18	CuCl/Cu(2.68/5.36)	BPy(5.36)	DMF(40)	26.8	80	2	6.80	6.09	
19	CuCl/Cu(2.68/5.36)	BPy(5.36)	DMF(40)	26.8	80	4	8.98	6.65	
20	CuCl/Cu(2.68/5.36)	BPy(5.36)	DMF(40)	26.8	80	6	9.47	7.29	
21	CuCl/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	42.9	80	1	1.35	7.05	
22	CuCl/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	42.9	80	2	2.46	7.41	
23	CuCl/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	42.9	80	4	4.22	8.62	
24	CuCl/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	42.9	80	6	5.72	8.74	
25	CuCl/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	42.9	80	8	5.91	9.49	
26	CuCl/Cu(1.07/2.14)	BPy(2.14)	NMP(40)	26.8	100	0.5	1.93	2.79	
27	CuCl/Cu(1.07/2.14)	BPy(2.14)	NMP(40)	26.8	100	1	4.88	3.56	
28	CuCl/Cu(1.07/2.14)	BPy(2.14)	NMP(40)	26.8	100	2	7.02	4.03	
29	CuCl/Cu(1.07/2.14)	BPy(2.14)	NMP(40)	26.8	100	4	8.00	5.05	
30	CuCl/Cu(1.07/2.14)	BPy(2.14)	NMP(40)	26.8	100	6	8.55	5.95	
31	CuCl/Cu(1.07/2.14)	PMDETA(1.07)	NMP(40)	26.8	100	0.5	8.94	2.29	
32	CuCl/Cu(1.07/2.14)	PMDETA(1.07)	NMP(40)	26.8	100	1	8.95	2.83	
33	CuCl/Cu(1.07/2.14)	PMDETA(1.07)	NMP(40)	26.8	100	2	10.37	3.74	
34	CuCl/Cu(1.07/2.14)	PMDETA(1.07)	NMP(40)	26.8	100	4	10.88	4.93	
35	CuCl/Cu(1.07/2.14)	PMDETA(1.07)	NMP(40)	26.8	100	6	10.50	6.39	
36	CuCl/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	10.7	80	0.5	1.19	3.92	
37	CuCl/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	10.7	80	1	2.41	6.03	
38	CuCl/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	10.7	80	2	4.94	6.97	
39	CuCl/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	10.7	80	4	7.15	7.36	
40	CuCl/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	10.7	80	6	8.48	8.40	
41	CuCl/Cu(2.68/5.36)	BPy(5.36)	NMP(40)	10.7	80	8	8.76	8.58	
42	CuCl/Cu(2.68/5.36)	BPy(5.36)	DMSO(40)	26.8	80	0.5	4.30	8.08	84.1
43	CuCl/Cu(2.68/5.36)	BPy(5.36)	DMSO(40)	26.8	80	1	7.23	8.84	
44	CuCl/Cu(2.68/5.36)	BPy(5.36)	DMSO(40)	26.8	80	2	8.21	9.64	69.3
45	CuCl/Cu(2.68/5.36)	BPy(5.36)	DMSO(40)	26.8	80	4	8.33	11.93	53.9
46	CuCl/Cu(2.68/5.36)	BPy(5.36)	DMSO(40)	26.8	80	6	8.49	12.64	56.8
47	CuCl/Cu(0.54/1.07)	BPy(1.07)	NMP(8)	5.36	100	6	0	0	

[a] *Conditions: P(VDF-co-CTFE) (80/20):2.0 g (Entry 1-46); PVDF: 0.4 g (Entry 47).*
[b] *The limiting viscosity of the copolymer was determined using typical Ubbelohde method in DMF at 30 °C.*

2. Thermal properties of thermally self-curable fluoropolymer.

Differential scanning calorimetry (DSC) analysis was employed to examine the thermal behavior of the polymers at different heating rate, as shown in Figure 1S. The Y-intercept obtained from the linear-fitted curve of the curing temperature obtained at different heating rates is regarded as the curing temperature of P(VDF-*co*-CTFE)-g-TEMPO, as shown in Figure 2S.



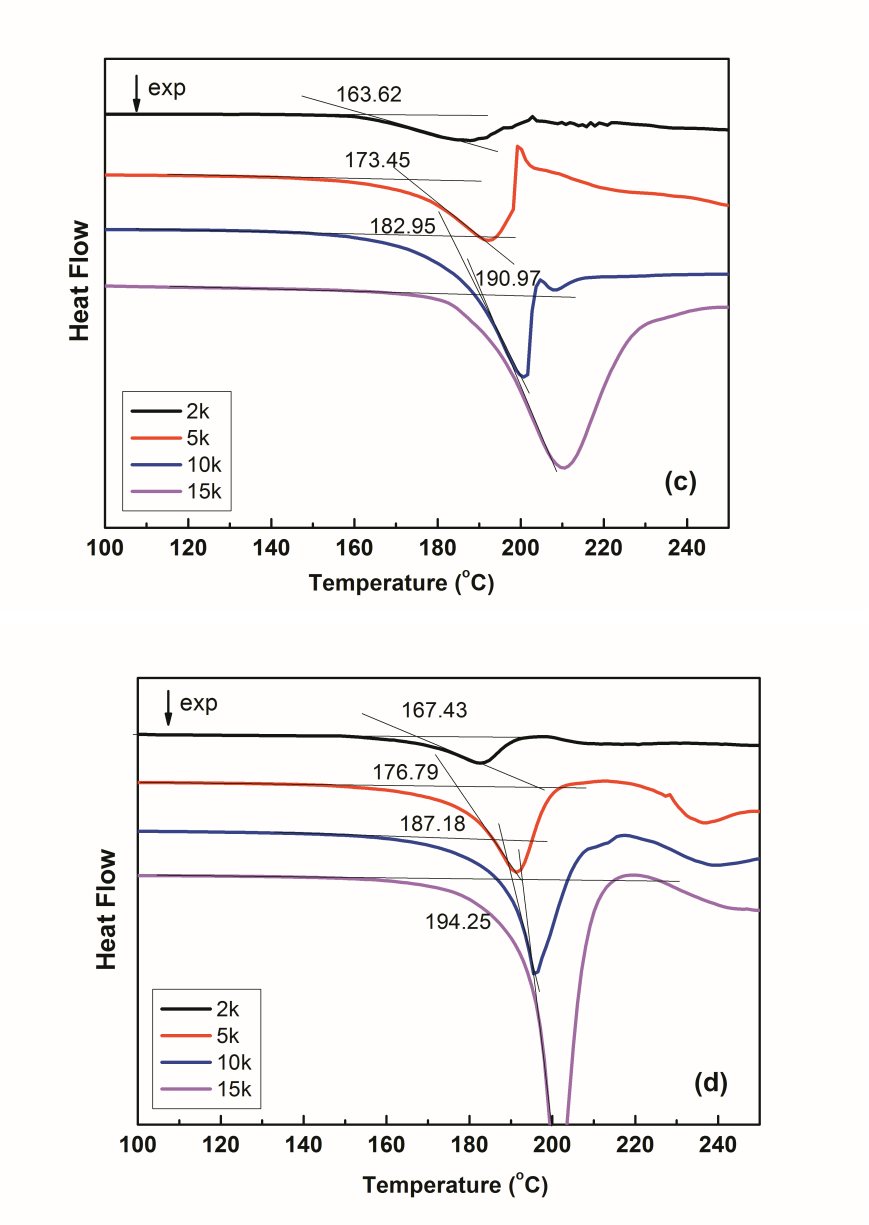


Figure 1S. DSC curves of product copolymers at different heating rate.(a-d: Sample 1-4).

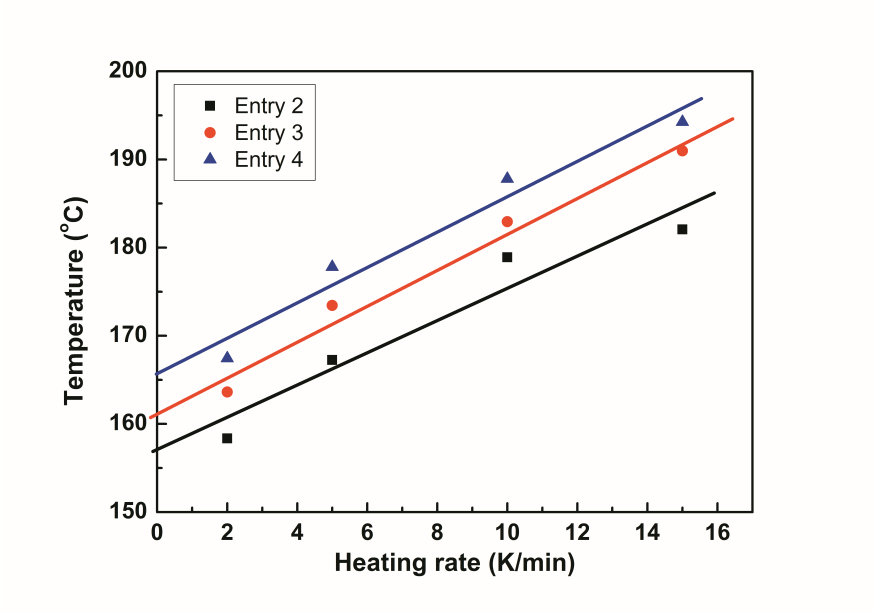


Figure 2S. The curves of curing temperature depends on heating rate.

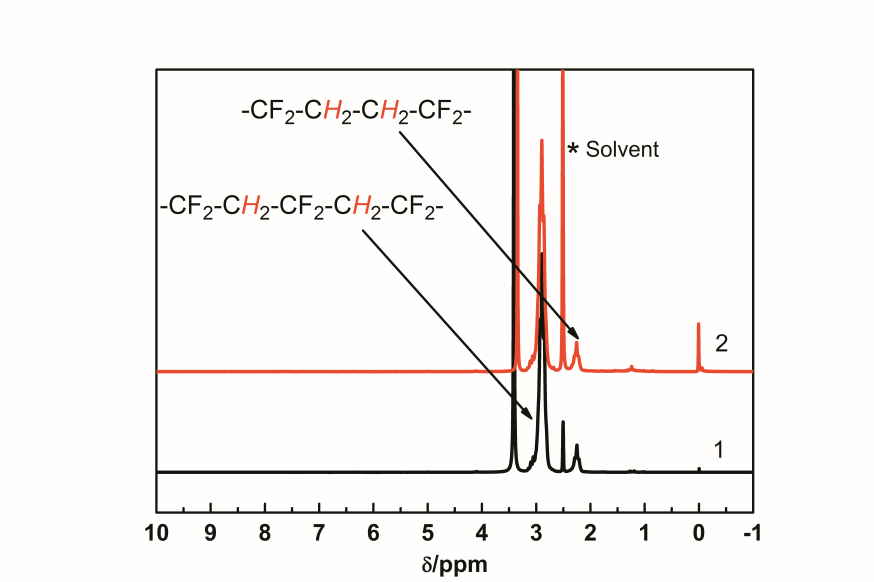


Figure 3S. ^{1}H NMR spectrum of PVDF before (line 1) and after reacted with CuCl/Cu/Bpy/TEMPO at 100 ^{o}C (line 2) in NMP for 6 h. (DMSO-d_6)