Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

A Multi-functional Chromone-modified Polyethylene via Metal-free C−H Activation

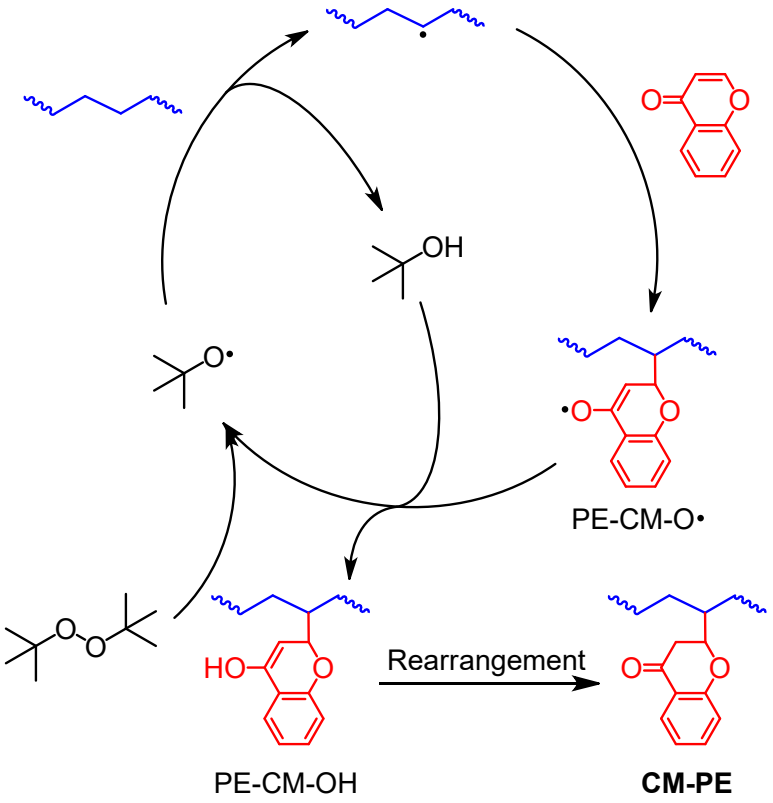
Yongjie Zhang[a,b], Xiaopei Li[a,b], Wenqin Zhu[c], Pibo Liu[a], Juntao Ren[a], Shangtao Chen[c], Yanming Hu[a]*, Guangyuan Zhou[a]*

[a] Division of Energy Materials, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

[b] Dalian Polytechnic University, Dalian 116034, China

[c] Petrochemical Research Institute, PetroChina, Beijing 102206, China

* Corresponding authors: Yanming Hu (ymhu@dicp.ac.cn) and Guangyuan Zhou (gyzhou@dicp.ac.cn)



1 tBuOOtBu $\xrightarrow{k_1}$ 2 tBuO•

2 tBuO• + PE-H $\xrightarrow{k_2}$ tBuOH + PE•

3 PE• + PE• $\xrightarrow{k_3}$ x-PE

4 PE• + CM $\xrightarrow{k_4}$ PE-CM-O•

5 PE-CM-O• + tBuOH $\xrightarrow{k_5}$ PE-CM-OH

6 PE-CM-OH $\xrightarrow{k_6}$ **CM-PE**

$k_3=k_c$
Rate of crosslinking:
$R_c=k_c[PE^*][PE^*]$

$k_4=k_f$
Rate of functionalization:
$R_c=k_c[PE^*][PE^*]$

Scheme S1 Proposed mechanism and elementary reactions for the synthesis of CM-PE

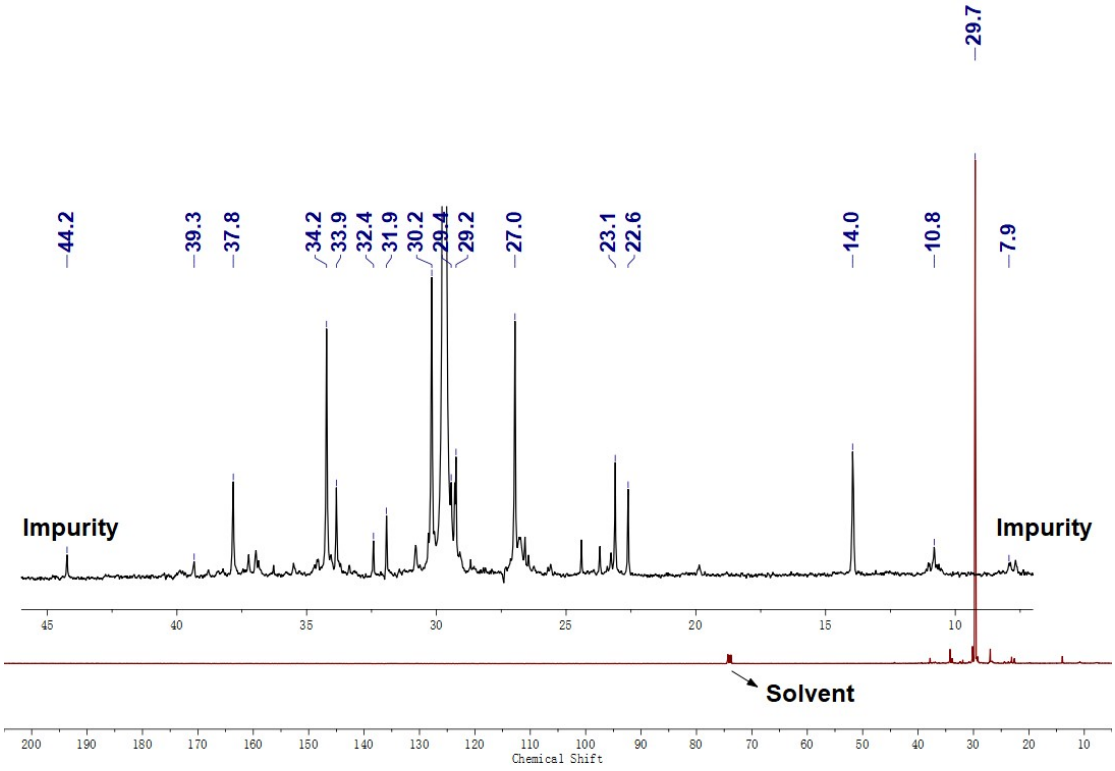
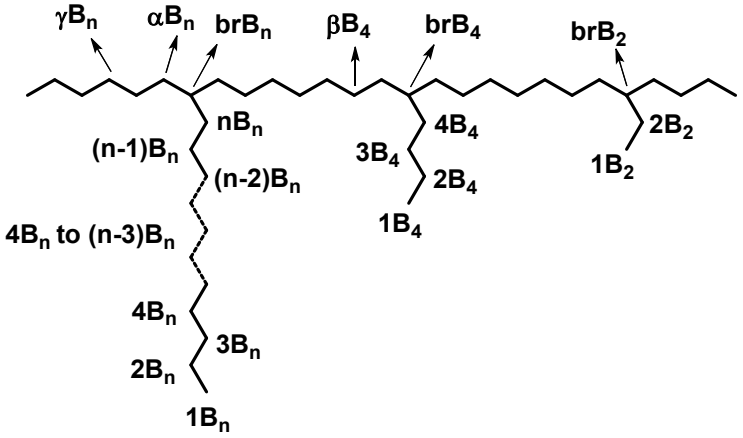


Figure S1 Typical ^{13}C NMR spectrum of precursor PE (1,1,2,2-tetrachloroethane-d2). Resonance peaks assigned according to the reference, *Macromolecules* 2002, 35, 2, 339–345. Detailed assignments were shown in **Table S1**.

Table S1 Carbon-13 chemical shifts and assignments for precursor PE



chemical shift (ppm)	assignments	chemical shift (ppm)	assignments
10.8	$1B_2$	29.7	CH_2 (main chain)
14.0	$1B_4$, $1B_n$ ($n \geqslant 6$)	30.2	γB_2, γB_4, γB_n, $(n-2)B_n$
22.6	$2B_n$	31.9	uncertain
23.1	$2B_4$	32.4	$3B_n$
27.0	$2B_2$, βB_2, βB_n, $(n-1)B_n$	34.2	αB_2, $4B_4$, αB_4, αB_n, nB_n
29.2	$3B_4$	37.8	brB_4, brB_n
29.4	$4B_n$	39.3	brB_2

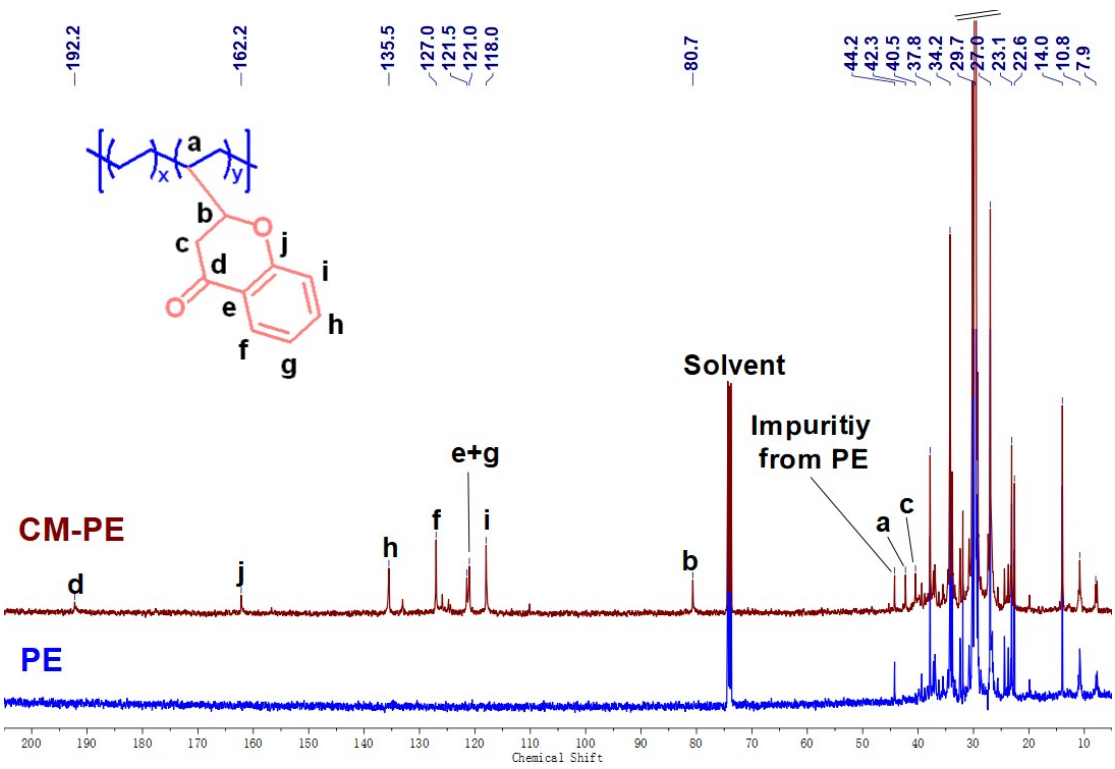


Figure S2 ^{13}C NMR spectra of the typical CM-PE (1,1,2,2-tetrachloroethane-d2, Entry 6 in Table 1) and the original PE.

Figure S3 Scale-up synthesis of hundreds grams of CM-PE under the solvent-free conditions

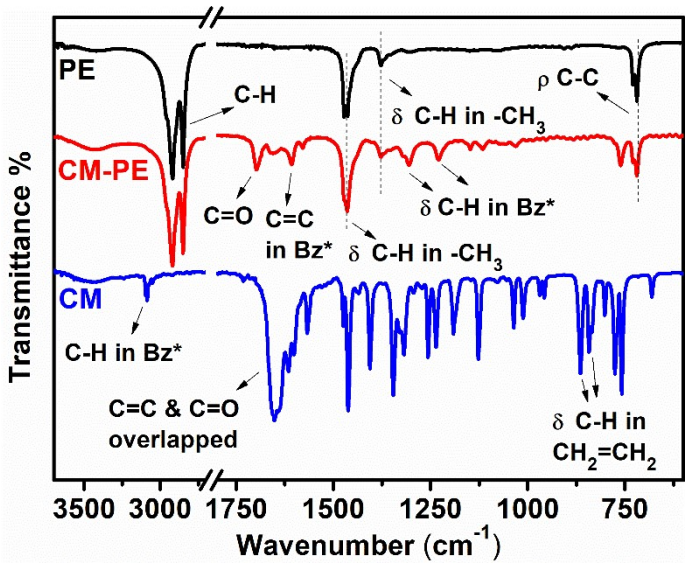


Figure S4 Typical FTIR spectra of PE, CM-PE, and chromone (CM). Symbols δ and ρ stand for bending and rocking, respectively. Absorption peaks without symbol are due to bond stretching. Characteristic peaks for PE, CM-PE, and chromone are listed in **Table S2**.

Table S2 Characteristic peaks for PE, CM-PE, and chromone in FTIR

Peak (cm^{-1})	Bond	Description	Sample
2919, 2850	C−H	Stretching	PE
1474, 1464	C−H	Bending, in CH_2	
1378	C−H	Bending, in CH_3	
720	C−C in $(CH_2)_n$, n>6	Rocking	
1698	C=O	Stretching	CM-PE
1607	C=C in benzene ring	Stretching	
1306, 1229	C−H in benzene ring	Bending	
3086	C−H in benzene ring	Stretching	
1652	C=C & C=O (overlapping due to conjuction)	Stretching	CM
865, 843	C−H in -CH=CH_2 (Disappeared in CM-PE)	Bending	

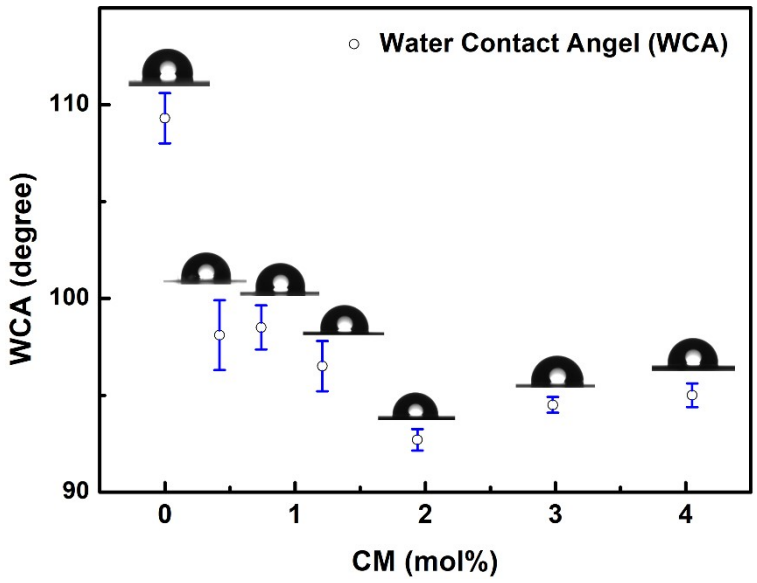


Figure S5 Water contact angles of parent PE and CM-PE

Table S3 Functionalization of PE with CM catalyzed by DTBP

Entry	T/°C	t/h	NAP.[a]	CM/DBTP /PE_{100}[b]	CM[c] (mol%)	M_n[d] (g/mol)	$Đ$[d]	ΔH_m[e] (J/g)	T_m (°C)	ΔH_c[e] (J/g)	T_c (°C)
PE	–	–	–	–	0	7460	2.30	65.9	100.5/105.0	64.3	90.8
1	140	1	1	10/5/1	1.21	8950	3.9	49.5	98.8	49.8	87.8
2	140	1	1	10/10/1	1.94	9570	8.8	44.4	91.8	39.0	76.8
3	140	1	1	15/10/1	1.57	8600	5.9	40.3	92.9	40.3	78.9
4	140	1	1	30/10/1	1.46	8760	4.7	42.5	93.2	41.3	78.6
5	140	1	1	50/10/1	0.74	7980	3.0	50.6	99.4	49.6	89.6
6	140	2	1	30/10/1	4.05	8850	6.8	48.0	93.2	46.9	79.4
7	140	1	3	50/10/1	0.61	8430	2.2	55.6	99.8	51.3	89.7
8	140	5	3	50/10/1	2.98	7430	4.4	34.7	87.5	33.1	72.1
9	125	6	1	30/10/1	0.50	7600	2.7	46.1	99.8	43.3	89.0
10	140	1	0	5/5/1	0.33	12300	4.6	49.7	98.7	49.9	88.2
11	140	1	0	10/5/1	0.42	11980	4.8	55.2	98.1	53.0	87.0
12	140	1	0	10/10/1	0.74	13050	20.0	52.9	94.4	57.1	81.2
13	140	1	0	15/10/1	1.09	13870	9.4	43.8	94.4	45.4	80.5
14	125	1	0	15/10/1	0.44	8190	2.3	59.0	100.8	69.4	89.1
15	130	1	1	30/10/1	0.53	7590	2.3	56.2	101.0	53.4	90.5
16	150	0.75	1	30/10/1	3.42	9240	7.6	34.4	90.4	34.5	74.4
17[f]	125	0.25	0	15/10/1	0.18	7440	1.8	57.9	101.0	52.7	90.5
18[f]	140	0.25	0	30/10/1	0.19	6840	1.9	61.9	90.4	54.4	74.4

[a] The weight ratios of naphthalene as a solvent to the precursor PE. [b] The molar ratios of CM and DTBP to 100 ethylene units. [c] CM graft ratio in

CM-PE. [d] GPC data. [e] ΔH_m and ΔH_c values were normalized to PE based on calculated weight ratios. [f] Reactive extrusion conditions.

Table S4 TGA data for PE and CM-PEs

Sample	$T_{5\%}$ (°C)	T_{onset} (°C)
PE	305.7	327.1
CM-PE0.50	329.4	371.1
CM-PE0.74	336.5	374.7
CM-PE1.21	334.4	372.4
CM-PE1.94	329.8	386.7
CM-PE2.98	331.7	391.2
CM-PE4.05	344.3	393.8
LDPE	297.9	318.4
LDPE/CM-PE4.05 Blend (90/10, w/w)	308.4	344.8

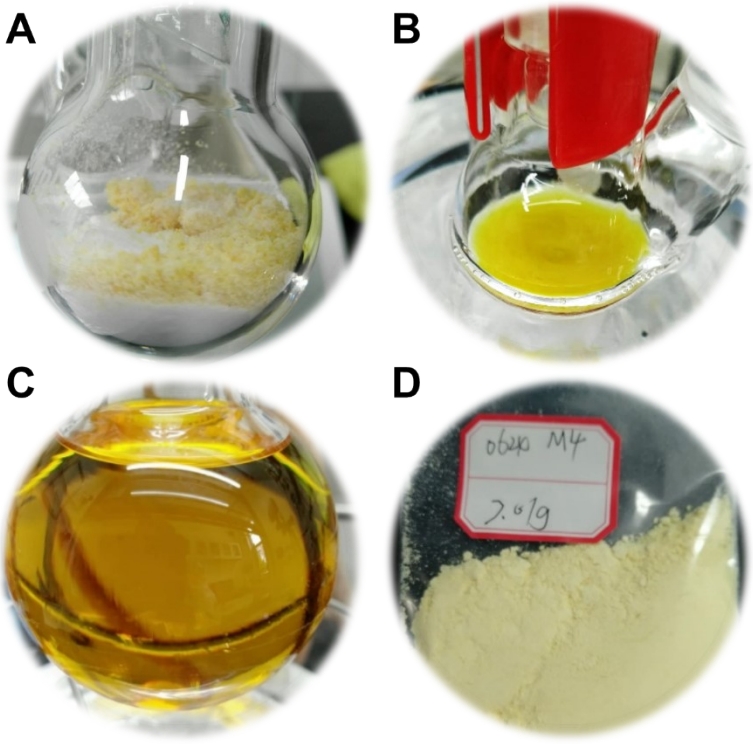


Figure S6 Digital pictures illustrating solvent- and metal-free C-H activation of PE.

(A) A mixture of PE and chromone.

(B) After PE and chromone melting down, DTBP was injected into the mixture to start the reaction.

(C) CM-PE was dissolved in hot xylene and precipitated later using cold methanol. Picture shows that CM-PE was completely soluble in xylene.

(D) Grams of CM-PE in a bright yellow powder form was synthesized.