Supporting Information for

Preparation of Functional Polyethenes by Catalytic Copolymerization

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Experimental

1. Materials. All manipulations for the synthesis of catalysts were done under argon using standard Shlenk techniques. Ligand **1** (2-[bis(2-metoxyphenyl)-phosphanyl]-4-benzenesulfonic acid and ligand **2** (2-[bis(phenyl)-phosphanyl]-4-benzenesulfonic acid and catalysts **1a**, **2a** and **2b** were prepared and characterized according to the literature (references 13 and 7). Solvents was purified by distillation over CaH_2 and degassed using three freeze-pump-thaw cycles and kept over activated molecular sieves. Maleic anhydride (MA) was purified by crystallization in benzene at 4°C. The resulting solid was washing 3 times with cold benzene and dried over night under vacuum. Acrylic acid (AA) was purified by vacuum distillation at 1 mm of Hg and 30°C over CaH_2. The AA was recovered at -78°C and degassed using three freeze-pump-thaw cycles. It was kept in the solid state for the rest of the experiments (-30°C). Carbic anhydride (CA) was prepared by combining cyclopentadiene and maleic anhydride in dichloromethane for 12 hours at room temperature. The resulting solid was filtered off, washed 3 times with cold diethyl ether and dried over night under vacuum. All the monomers were kept in the glove box.

2. Polymerization procedures. Depending on the volume of solvent and reaction pressure, polymerizations were carried out in a stainless steel reactor (400 mL or 100 mL, Parr) at pressures comprised between 100 and 320 psi. In a N_2 filled glove box, all reagents were combined in the reactor. The reactor was then connected to a monitoring station outside the drybox, it was heated to the desired temperature, and the mixture stirred with a four-blade impeller at 800 rpm.

2.1 Typical procedure for MA copolymerization. In the vessel, 21 mg of catalyst **1a** (3.5 x 10^{-5} mol) and 20 g of MA (0.20 mL) were added to 130 ml of toluene and 50 ml of diethyl ether containing 2 mg of 2,6-di-*tert*-butyl-4-methylphenol (BHT). After 15 h of reaction time at 95°C under 300 psi of ethylene pressure, the reactor was cooled down to room temperature and slowly depressurized. The polymers were precipitated in four volumes of cold acetone, collected by centrifugation or filtered, washed 3 times with cold acetone and 3 times with cold diethyl ether, and dried under vacuum.

2.2 Typical procedure for CA copolymerization. In the vessel, 7.5 mg of catalyst **1a** (1.2 x 10^{-5} mol), 4.2 g of monomer (0.026 mol) were added to 45 ml of toluene containing 2 mg of 2,6-di-*tert*-butyl-4-methylphenol (BHT). The reactor was immediately pressurized at 115 psi, stirred at 800 rpm and heated to 90 °C. After 6 h, the reactor was cooled down to

room temperature and slowly depressurized. The polymers were precipitated in four volumes of cold acetone, collected by centrifugation and filtered, washed 3 times with cold acetone and dried under vacuum.

2.3 Typical procedure for AA copolymerization. In the vessel, 8.0 mg of catalyst **2b** (1.4 x 10^{-5} mol), 1.0 g of monomer (0.014 mol) were added to 50 ml of toluene. The reactor was was immediately pressurized at 100 psi, stirred at 800 rpms and heated to 75 ^{o}C. After 15 h, the reactor was cooled down to room temperature and slowly depressurized. The polymers were precipitated in four volumes of methanol containing 10% volume of H_2O, collected by centrifugation, washed 3 times with the methanol-H_2O mixture and 3 times with deuterated methanol and left to dry in air overnight (in a fume hood). The washing steps were necessary to remove AA homopolymer produced by self-initiated radical polymerization at high temperature (Polyacrylic acid is soluble in methanol and water). Furthermore, in a control experiment, it was checked that no copolymer was produced when the catalyst was not present.

3. Characterization

3.1 GPC

The molecular weight distributions were determined by gel permeation chromatography (GPC) using a Viscotek HT GPC equipped with triple detection operating at 160 ^{o}C. The eluent was 1,2,4-trichlorobenzene, and separation was performed on three PolymerLabs Mixed B(-LS) columns. The dn/dc of pure linear polyethylene was found to be 0.106 mL/g at this temperature. Owing to the fact that the copolymers have low incorporations in polar monomer, their dn/dc was approximated to the one of pure PE. We found that polymers bearing COOH groups had a tendency to deteriorate the GPC columns (as shown by a pressure increase), therefore, GPC analysis results are not reported for copolymers of AA.

3.2 FTIR

The solid polymers FTIR spectra were recorded on a Nicolet 6700 Spectrometer equipped with Smart ATR accessory (ThermoSci).

3.3 DSC

Differential scanning calorimetry measurements (DSC) of solid samples were performed on a DSC823e (TOPEM modulation) equipped with an FRS5 sample cell, a sample robot, a Julabo FT400 intracooler and an HRS7 sensor from Mettler Toledo. Samples were heated from 20^{o}C to 140^{o}C at a rate of 0.3 ^{o}C/minute and data were analyzed with STAR software. The amplitude of TOPEM modulation was 0.025K, using switching times comprised between 15 and 30 seconds. All reported values are for samples which have first been slowly cooled from the melt at a rate of 0.3 ^{o}C/minute, except for the CA containing copolymer (entry 4 in Table 1), for which the melting point was only observed for the first heating cycle (prior cooling). Owing to the high insertion of CA in the copolymer, this sample is nearly totally amorphous and does not crystallize after being melted. The content of crystallinity was obtained from the enthalpy of melting, which was normalized by the heat of melting of a 100% crystalline PE sample (294 J/g).

3.4 NMR

All the NMR spectra were recorded on Varian 600 MHz (Inova). NMR spectra of the polymers with AA or MA were recorded in tetrachloroethane-d_2 (TCE) at 90^{o}C and

115°C. The NMR spectra for the polymers with CA were recorded in toluene-d_6 90 °C. For ^{13}C spectra (10000 scans), an ungated decoupling sequence with a pulse angle of 20° and a delay of 10s between two scans was used in order to ensure quantitative measurements. For both CA and MA containing copolymers, significant decomposition occurred during the accumulation of the ^{13}C sample (likely due to hydrolysis by ambient humidity at high temperature).
For the CYCLENOE sequence (64 scans), a pulse angle of 20° and a delay of 10s between two scans was used in order to ensure quantitative measurements, the control was at -952.8 Hz, saturation frequency at -2403.4 Hz (1.7 ppm) with a time of 4.0s and a mixing time of 0.010s.
Stability of catalyst 1b. This study was performed by recording ^1H NMR spectra of catalyst **1b** (7.7×10^{-5} mol) in $CDCl_3$ containing 12 µl of degassed AA at 25, 40 and 50 °C. The sample was kept at 50 °C for 8 hours before the recorded of the spectra again.

3.5 MALDI TOF mass spectrometry. The Matrix-Assisted Laser Desorption-Ionization Time-Of-Flight instrument (M@LDI, from Waters Micromass) used a nitrogen laser (337 nm) and accelerating voltage of 20 kV. The copolymers were premixed in THF or in dichlorobenzene at a concentration of 1 g/L (the solution being not completely homogeneous). In the sample wells, two successive depots were made, first of the matrix (1 µl of a solution of sinnapic acid in THF at 10 g/L), then of the polymer solution (1 µl). Care was taken to make both depots rapidly enough in order the solvent of the first depot not to evaporate before the second depot was made. After both depots were made, the sample wells were left to dry. The positive ions were detected in reflectron mode (no cationizing agent added). Each spectrum was the sum of several minutes of continuous accumulation (300 target shoots).

Copolymer of ethylene and AA

Assignation of the resonances for this copolymer was based on the data published for copolymers prepared by hydrolysis of poly(ethylene-co-*tert*-butyl acrylate) (reference 6).

Calculation of the molar incorporation x of AA

I_A : integral of methine proton A - I_{chain} : integral of protons B, B', C and all other main chain protons

$$x = \frac{4I_A}{I_{rest} + 2I_A}$$

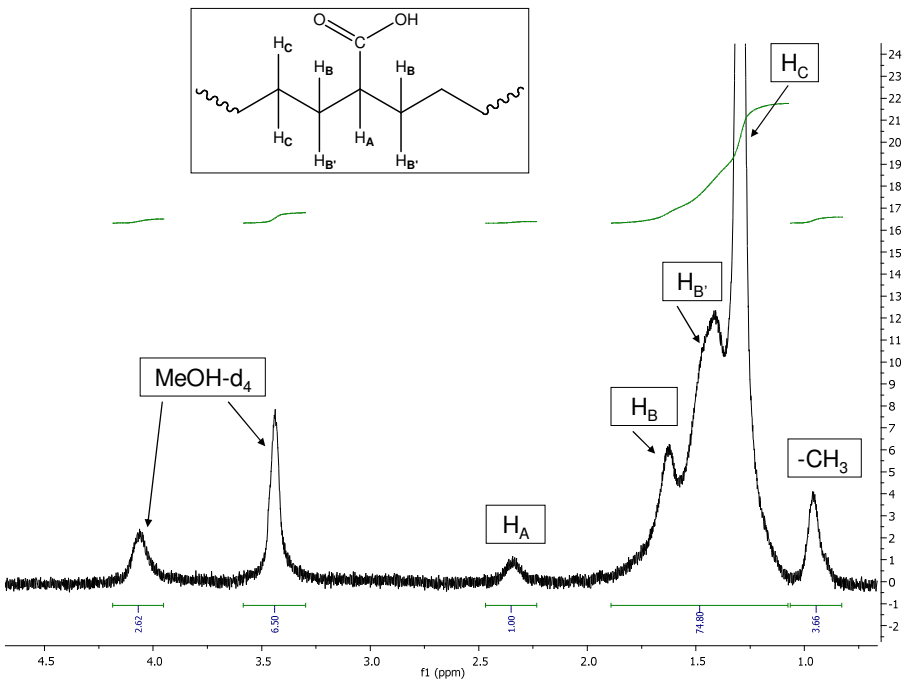
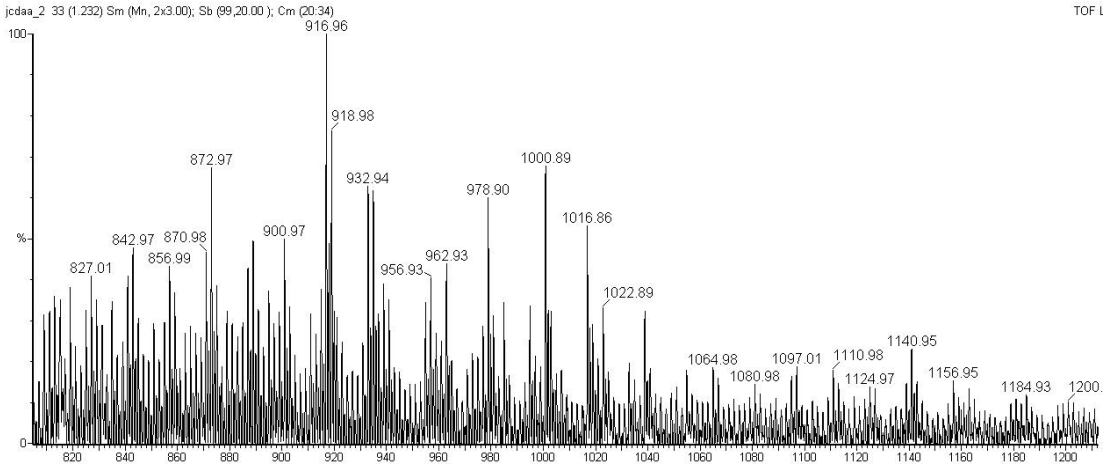


Figure 1a. ^{1}H NMR of poly(ethylene-co-AA) with 5 mol% of AA. ($C_2D_2Cl_4$, T = 115 ^{o}C).

1H NMR (600 MHz, T = 115 ^{o}C, TCE-d_2, δ): 2.3 (m, 1H, C**H**COOH), 1.6 (m, 2H, C**H$_B$**H$_B$'CHCOOHC**H$_B$**H$_B$'), 1.4 (m, 2H, CH$_B$**H$_B$'**CHCOOHCH$_B$**H$_B$'**), 1.2-1.3 (m, C**H$_2$**), 0.9 (m, -C**H$_3$**, end chain)

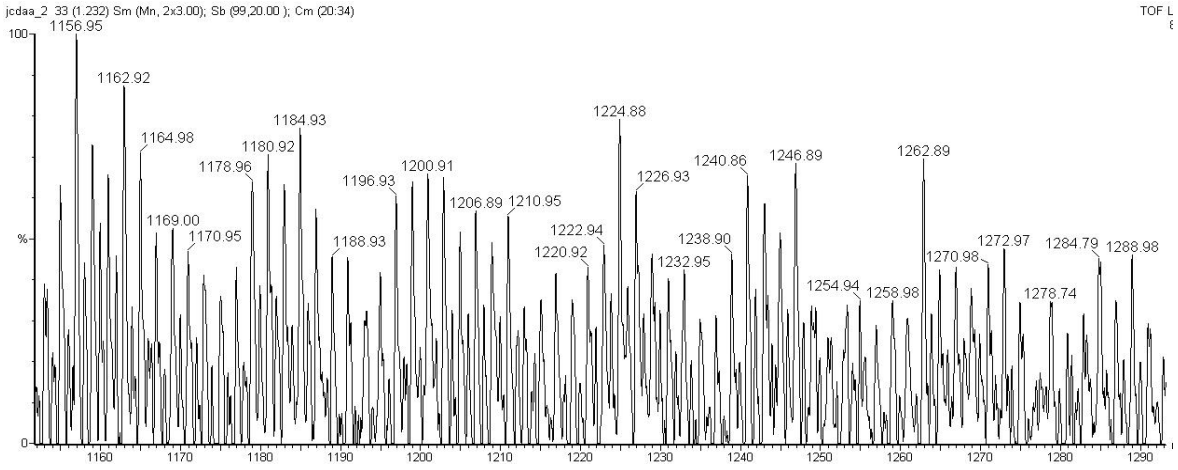
Figure 1b. MALDI-TOF MS of copolymers of AA with ethylene.



Attribution :
HExAAy (resp CExAAy) indicates a chain of x ethylene units,
y AA units and initiated by a hydride (respectively a methyl group)

m/z	structure
872.97	$HE_{26}AA_2$
900.97	$HE_{27}AA_2$
916.96	$HE_{25}AA_3$
932.94	$HE_{23}AA_4$
978.90	$CE_{19}AA_2$
1000.89	$HE_{28}AA_3$
1016.86	$HE_{26}AA_4$

Figure 1c. MALDI-TOF MS of copolymers of AA with ethylene.



Attribution

m/z	structure
1169.00	$HE_{34}AA_3$
1170.95	$CE_{31}AA_4$
1178.96	$HE_{39}AA_3$
1180.92	$HE_{36}AA_1$
1184.93	$HE_{32}AA_4$
1188.93	$CE_{34}AA_3$
1196.83	$HE_{35}AA_3$
1200.91	$HE_{30}AA_4$
1206.89	$CE_{40}AA_1$
1210.95	$CE_{35}AA_3$
1224.88	$HE_{36}AA_3$
1226.93	$CE_{33}AA_4$
1240.86	$CE_{36}AA_3$

To identify each peak, the following tables were prepared:

n	HEnAA1	HEnAA2	HEnAA3	HEnAA4	HEnAA5	HEnAA6	HEnAA7
10,00	352,33	424,36	496,38	568,40	640,42	712,44	784,46
11,00	380,37	452,39	524,41	596,43	668,45	740,47	812,49
12,00	408,40	480,42	552,44	624,46	696,48	768,50	840,52
13,00	436,43	508,45	580,47	652,49	724,51	796,53	868,55
14,00	464,46	536,48	608,50	680,52	752,54	824,56	896,59
15,00	492,49	564,51	636,53	708,55	780,58	852,60	924,62
16,00	520,52	592,54	664,56	736,59	808,61	880,63	952,65
17,00	548,55	620,57	692,60	764,62	836,64	908,66	980,68
18,00	576,58	648,61	720,63	792,65	864,67	936,69	1 008,71
19,00	604,62	676,64	748,66	820,68	892,70	964,72	1 036,74
20,00	632,65	704,67	776,69	848,71	920,73	992,75	1 064,77
21,00	660,68	732,70	804,72	876,74	948,76	1 020,78	1 092,81
22,00	688,71	760,73	832,75	904,77	976,79	1 048,82	1 120,84
23,00	716,74	788,76	860,78	932,80	1 004,83	1 076,85	1 148,87
24,00	744,77	816,79	888,81	960,84	1 032,86	1 104,88	1 176,90
25,00	772,80	844,82	916,85	988,87	1 060,89	1 132,91	1 204,93
26,00	800,83	872,86	944,88	1 016,90	1 088,92	1 160,94	1 232,96
27,00	828,87	900,89	972,91	1 044,93	1 116,95	1 188,97	1 260,99
28,00	856,90	928,92	1 000,94	1 072,96	1 144,98	1 217,00	1 289,02
29,00	884,93	956,95	1 028,97	1 100,99	1 173,01	1 245,03	1 317,06
30,00	912,96	984,98	1 057,00	1 129,02	1 201,04	1 273,07	1 345,09
31,00	940,99	1 013,01	1 085,03	1 157,05	1 229,08	1 301,10	1 373,12
32,00	969,02	1 041,04	1 113,06	1 185,09	1 257,11	1 329,13	1 401,15
33,00	997,05	1 069,08	1 141,10	1 213,12	1 285,14	1 357,16	1 429,18
34,00	1 025,09	1 097,11	1 169,13	1 241,15	1 313,17	1 385,19	1 457,21
35,00	1 053,12	1 125,14	1 197,16	1 269,18	1 341,20	1 413,22	1 485,24
36,00	1 081,15	1 153,17	1 225,19	1 297,21	1 369,23	1 441,25	1 513,27
37,00	1 109,18	1 181,20	1 253,22	1 325,24	1 397,26	1 469,28	1 541,31
38,00	1 137,21	1 209,23	1 281,25	1 353,27	1 425,30	1 497,32	1 569,34
39,00	1 165,24	1 237,26	1 309,28	1 381,31	1 453,33	1 525,35	1 597,37
40,00	1 193,27	1 265,29	1 337,32	1 409,34	1 481,36	1 553,38	1 625,40
41,00	1 221,30	1 293,33	1 365,35	1 437,37	1 509,39	1 581,41	1 653,43
42,00	1 249,34	1 321,36	1 393,38	1 465,40	1 537,42	1 609,44	1 681,46
43,00	1 277,37	1 349,39	1 421,41	1 493,43	1 565,45	1 637,47	1 709,49
44,00	1 305,40	1 377,42	1 449,44	1 521,46	1 593,48	1 665,50	1 737,53
45,00	1 333,43	1 405,45	1 477,47	1 549,49	1 621,51	1 693,54	1 765,56
46,00	1 361,46	1 433,48	1 505,50	1 577,52	1 649,55	1 721,57	1 793,59
47,00	1 389,49	1 461,51	1 533,53	1 605,56	1 677,58	1 749,60	1 821,62

n	CEnAA1	CEnAA2	CEnAA3	CEnAA4	CEnAA5	CEnAA6	CEnAA7
10	366,33	438,36	510,38	582,40	654,42	726,44	798,46
11	394,37	466,39	538,41	610,43	682,45	754,47	826,49
12	422,40	494,42	566,44	638,46	710,48	782,50	854,52
13	450,43	522,45	594,47	666,49	738,51	810,53	882,55
14	478,46	550,48	622,50	694,52	766,54	838,56	910,59
15	506,49	578,51	650,53	722,55	794,58	866,60	938,62
16	534,52	606,54	678,56	750,59	822,61	894,63	966,65
17	562,55	634,57	706,60	778,62	850,64	922,66	994,68
18	590,58	662,61	734,63	806,65	878,67	950,69	1022,71
19	618,62	690,64	762,66	834,68	906,70	978,72	1050,74
20	646,65	718,67	790,69	862,71	934,73	1006,75	1078,77
21	674,68	746,70	818,72	890,74	962,76	1034,78	1106,81
22	702,71	774,73	846,75	918,77	990,79	1062,82	1134,84
23	730,74	802,76	874,78	946,80	1018,83	1090,85	1162,87
24	758,77	830,79	902,81	974,84	1046,86	1118,88	1190,90
25	786,80	858,82	930,85	1002,87	1074,89	1146,91	1218,93
26	814,83	886,86	958,88	1030,90	1102,92	1174,94	1246,96
27	842,87	914,89	986,91	1058,93	1130,95	1202,97	1274,99
28	870,90	942,92	1014,94	1086,96	1158,98	1231,00	1303,02
29	898,93	970,95	1042,97	1114,99	1187,01	1259,03	1331,06
30	926,96	998,98	1071,00	1143,02	1215,04	1287,07	1359,09
31	954,99	1027,01	1099,03	1171,05	1243,08	1315,10	1387,12
32	983,02	1055,04	1127,06	1199,09	1271,11	1343,13	1415,15
33	1011,05	1083,08	1155,10	1227,12	1299,14	1371,16	1443,18
34	1039,09	1111,11	1183,13	1255,15	1327,17	1399,19	1471,21
35	1067,12	1139,14	1211,16	1283,18	1355,20	1427,22	1499,24
36	1095,15	1167,17	1239,19	1311,21	1383,23	1455,25	1527,27
37	1123,18	1195,20	1267,22	1339,24	1411,26	1483,28	1555,31
38	1151,21	1223,23	1295,25	1367,27	1439,30	1511,32	1583,34
39	1179,24	1251,26	1323,28	1395,31	1467,33	1539,35	1611,37
40	1207,27	1279,29	1351,32	1423,34	1495,36	1567,38	1639,40

Copolymers of ethylene and MA

Assignation of the resonances for this copolymer was based on the following publications: Komber, H. *Macromol. Chem. Phys.* **1995**,196, 669-678, Drent, E. et al. *Chem Commun.* **2002**, 744, Yang, L. et al. *Macromolecules*, **2003**, 36 (13), 4709-4718 and Skupov, K. M. et al. *Macromolecules*, **2008**, 41 (7), 2309-2310

The copolymers of ethylene and MA are reactive, and have a tendency to undergo facile hydrolysis at high temperature with traces of moistures. The hydrolysis products were observed in all cases (see Figure 2a). One of the polymers was purposefully hydrolyzed (in acetone – H_2O) (see Figure 2b-2c). Furthermore, polymers prepared in diethyl ether (used to solubilize MA) contained significant MA end-groups (Figure 2a).

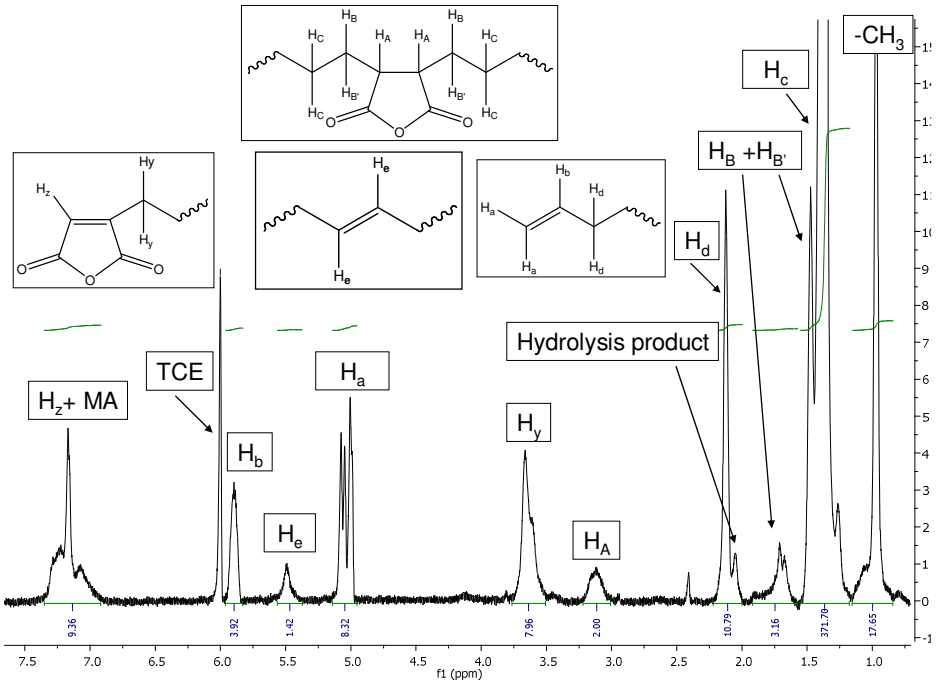


Figure 2a. ^{1}H NMR of poly(ethylene-co-MA) with 4 mol% of MA (entry 1 in Table 1). ($C_2D_2Cl_4$, T = 115 ^{o}C).

^{1}H NMR (600 MHz, T = 115 ^{o}C, TCE-d_2, δ): 7.2 (m, 1H, C**H**=CCH_2), 5.9 (m, 1H, CH_2=C**H**CH_2), 5.5 (m, 2H, CH_2C**H**=C**H**CH_2), 5.0 (m, 2H, C$\mathbf{H_2}$=CHCH_2), 3.7 (m, 2H, CH=CC$\mathbf{H_2}$), 3.1 (m, 2H, C**H**COOCOC**H**), 2.1 (m, 2H, CH_2=CHC$\mathbf{H_2}$)1.8-1.5 (m, 2H, C$\mathbf{H_2}$CHCH), 1.4-1.2 (m, C$\mathbf{H_2}$), 0.9 (m, -C$\mathbf{H_3}$ end chain);

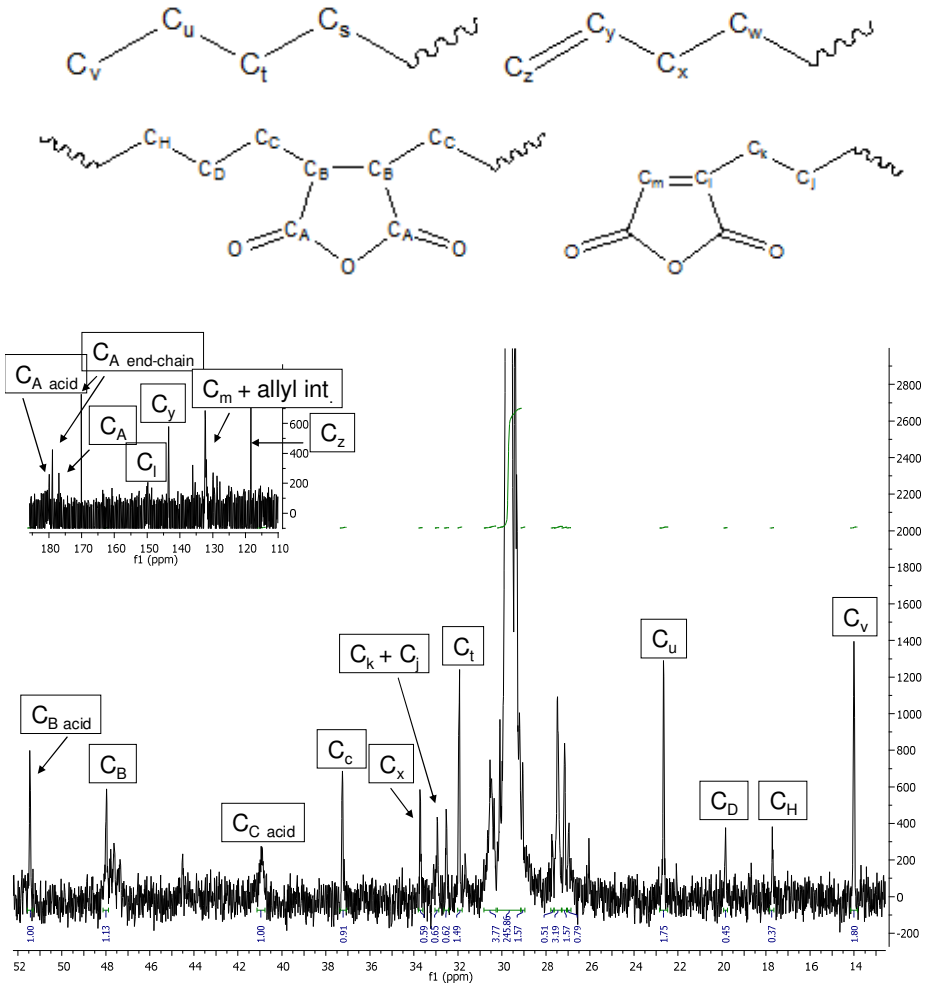


Figure 2b. ^{13}C NMR of poly(ethylene-co-MA) with 2 mol% of MA (entry 2 in Table 1). ($C_2D_2Cl_4$, T = 90 ^oC, 5000 scans).

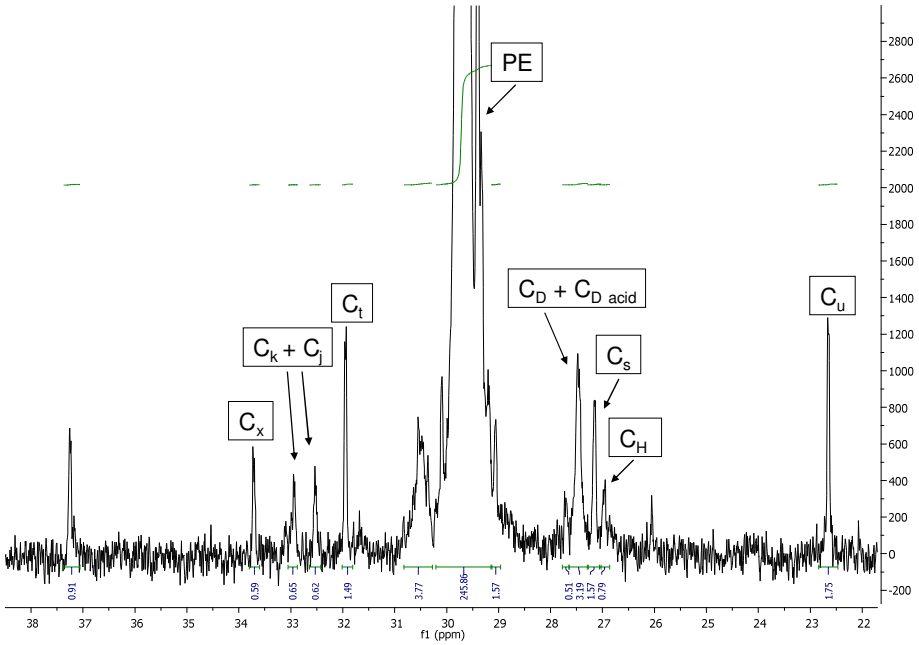


Figure 2c. ^{13}C NMR of poly(ethylene-co-MA) with 2 mol% of MA, zoom from 22 ppm to 35 ppm. (entry 2 in Table 1). ($C_2D_2Cl_4$, T = 90 ^oC, 5000 scans).

^{13}C NMR (121 MHz, T = 90 ^oC, $C_2D_2Cl_4$-d_2, δ): 175.8 ($C{=}O_{end\text{-}chain}$), 174.7 ($C{=}O_{acid}$), 172.7 ($C{=}O_{end\text{-}chain}$), 165.9 (C=O), 149.5 ($CH_2\mathbf{C}{=}CHC{=}O_{end\text{-}chain}$), 139.2 ($CH_2{=}\mathbf{C}HCH_2$), 128.1 ($CH_2C{=}\mathbf{C}HC{=}O_{end\text{-}chain}$ and allyl int.), 114.9 ($\mathbf{C}H_2{=}CHCH_2$), 51.5 ($CH_2\mathbf{C}HC{=}O_{acid}$), 48.0 ($CH_2\mathbf{C}HC{=}O$), 40.9 ($\mathbf{C}H_2CHC{=}O_{acid}$), 37.2 ($\mathbf{C}H_2CHC{=}O$), 33.7 ($CH_2{=}CH\mathbf{C}H_2$), 32.9 ($CH_2\mathbf{C}H_2C{=}CHC{=}O_{end\text{-}chain}$), 32.5 ($\mathbf{C}H_2CH_2C{=}CHC{=}O_{end\text{-}chain}$), 31.9 ($CH_3CH_2\mathbf{C}H_2CH_2$), 30.5-28.7 ($\mathbf{C}H_2$, PE), 27.5 ($\mathbf{C}H_2CH_2CHC{=}O$ and $\mathbf{C}H_2CH_2CHC{=}O_{acid}$), 27.2 ($CH_3CH_2CH_2\mathbf{C}H_2$), 22.7 ($CH_3\mathbf{C}H_2CH_2CH_2$), 19.9 ($\mathbf{C}H_2CH_2C{=}CHC{=}O_{end\text{-}chain}$), 17.7 ($\mathbf{C}H_2CH_2CH_2C{=}CHC{=}O_{end\text{-}chain}$), 14.0 ($\mathbf{C}H_3CH_2CH_2CH_2$)

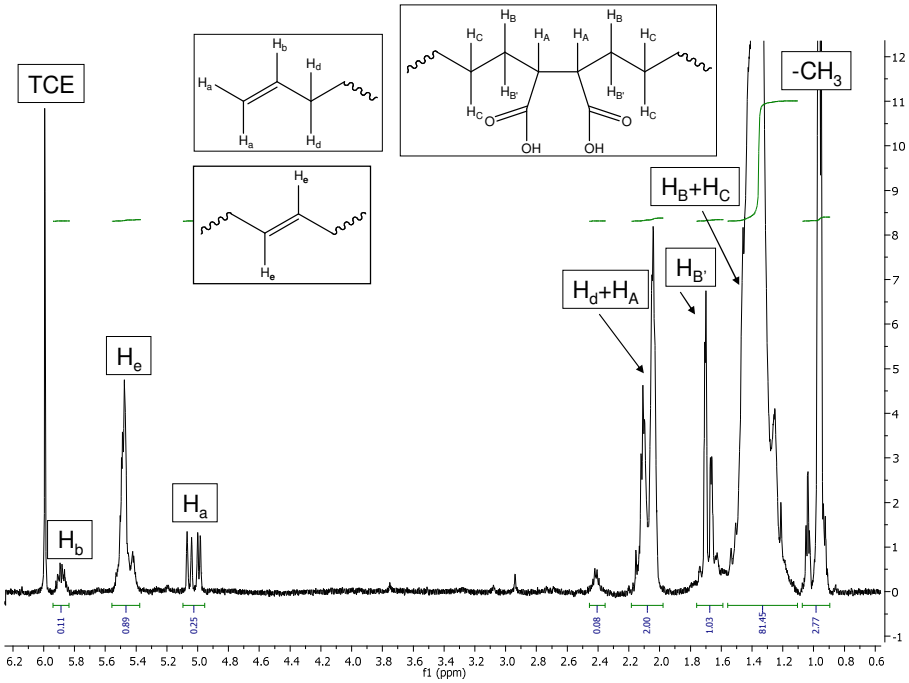


Figure 2d. ^{1}H NMR of poly(ethylene-co-*hydrolyzed*-MA) with 9 mol% of MA (entry 3 in Table 1). ($C_2D_2Cl_4$, T = 115 ^{o}C). No MA end-groups were detected (no peaks above 6.0)

1H NMR (600 MHz, T = 115 ^{o}C, TCE-d_2, δ): 5.9 (m, 1H, CH_2=C**H**CH_2), 5.5 (m, 2H, CH_2C**H**=C**H**CH_2), 5.0 (m, 2H, C$\mathbf{H_2}$=$CHCH_2$), 2.1-2.0 (m, 2H, CH_2=CHC$\mathbf{H_2}$), 2.1-2.0 (m, 2H, COOHC**H**C**H**COOH), 1.7 (m, 1H, C$\mathbf{H_B}$·CH_BCHCH), 1.4-1.2 (m, 1H, CH_B·C$\mathbf{H_B}$CHCH), 1.4-1.2 (m, C$\mathbf{H_2}$), 0.9 (m, -C$\mathbf{H_3}$ end chain);

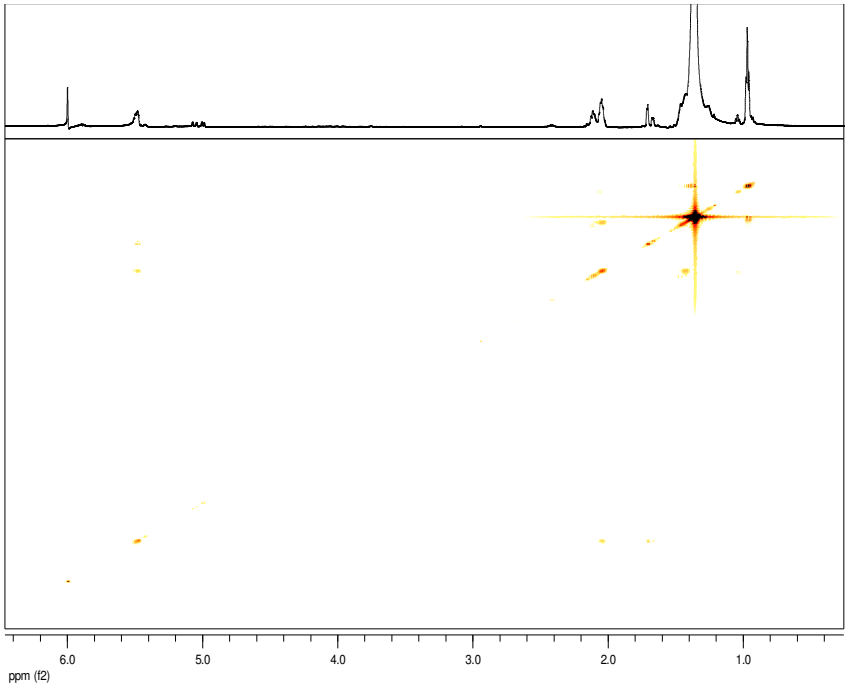


Figure 2c. COSY of poly(ethylene-co-*hydrolyzed*-MA) with 9 mol% of MA. ($C_2D_2Cl_4$, T = 115 ^oC).

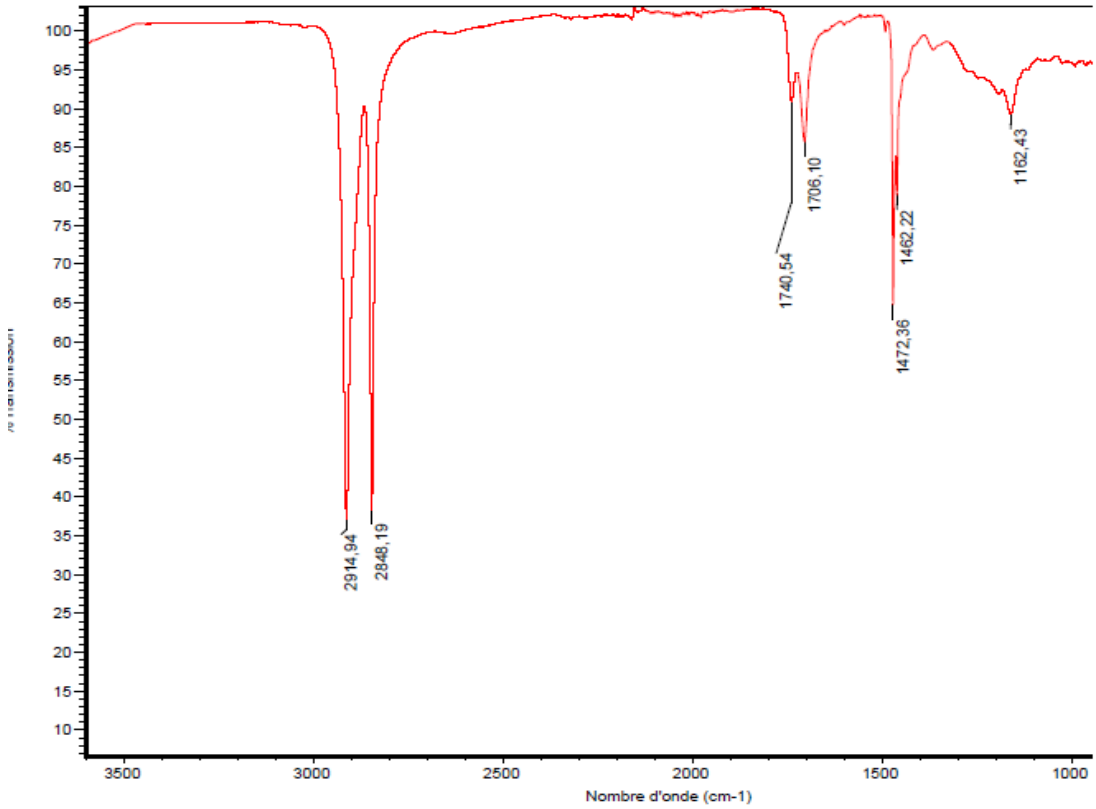
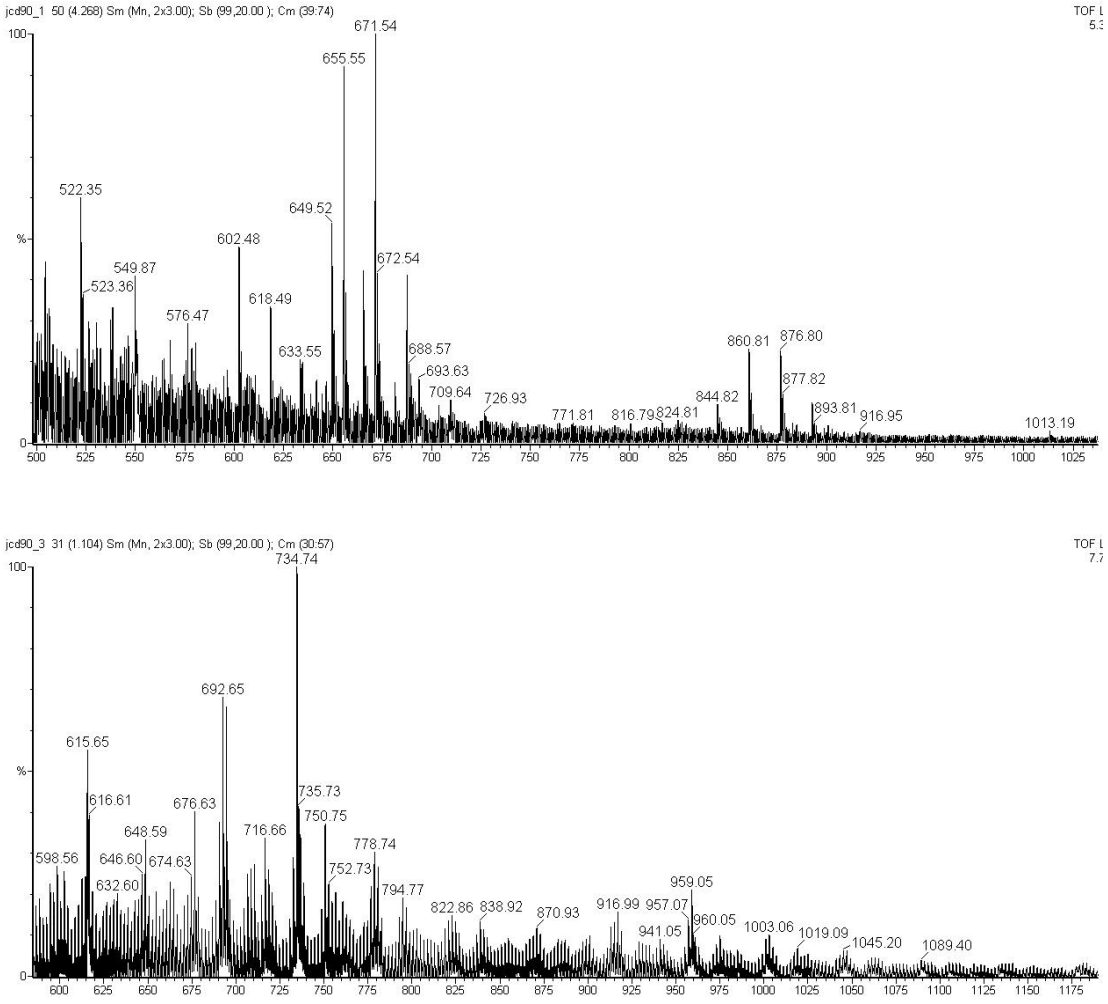


Figure 2d. FTIR (ATR) of poly(ethylene-co-MA) with 4 mol% of MA.

Assignations are based on Yang, L.; Zhang, F.; Endo, T.; Hirotsu T. *Macromolecules*, **2003**, 36, 4709-4718

IR (ATR): ν = 2914.9 (m, CH_2, stretch), 2848.1 (m, CH_2, stretch), 1740.5 (m, C=O, strech), 1706.1 (m, C=O, strech of hydrolyzed MA, COOH), 1472.4 (s, CH_2, scissor), 1462.2 (m, CH_2, scissor) 1162 (w, CH_2, wag).

Figure 2e. MALDI-TOF MS of copolymers of MA with ethylene (for illustrative purpose only). No structural information could be obtained from these spectrograms, likely because the MA units are partially hydrolyzed.



Copolymers of ethylene and CA

Assignations are based on Tritto, I. et al. *Macromolecules*, **2000**, 33 (24), 8931-8944

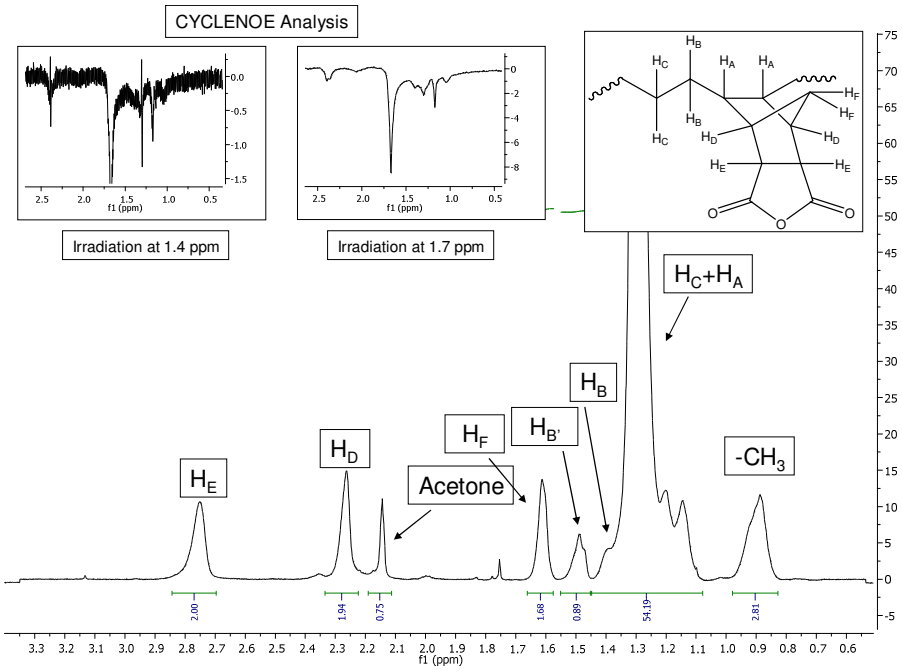


Figure 3a. ^{1}H NMR of poly(ethylene-co-CA) with 7 mol% of CA.

^{1}H NMR (600 MHz, T = 90 ^{o}C, Toluene-d_8, δ): 2.8 (m, 2H, C**H**COOCOC**H**), 2.2 (m, 2H, C**H**CH$_2$C**H**), 1.6 (m, 2H, CHC**H$_2$**CH), 1.5-1.4 (m, 2H, C**H$_2$**CHCH), 1.2-1.3 (m, C**H$_2$**), 1.3-1.2 (m, 2H, CH$_2$C**H**C**H**) 0.9 (m, -C**H$_3$**, end chain)

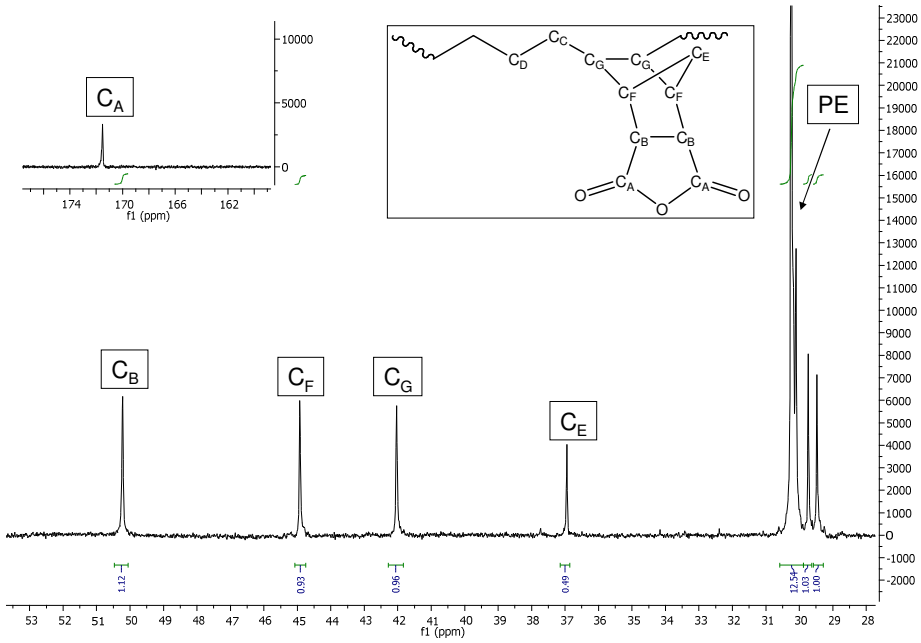


Figure 3b. ^{13}C NMR of poly(ethylene-co-CA) with 7 mol% of CA.

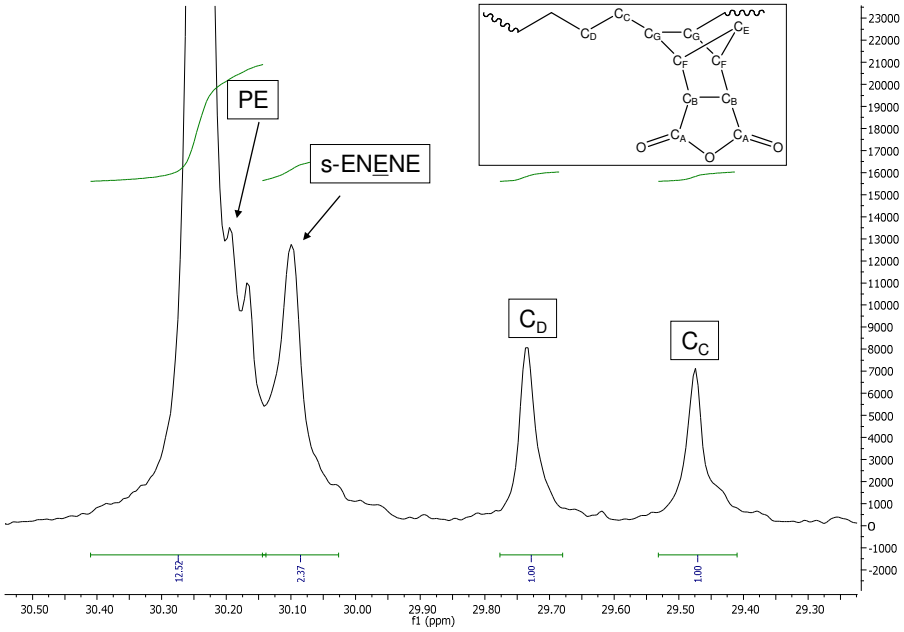


Figure 3c. ^{13}C NMR of poly(ethylene-co-CA) with 7 mol% of CA, zoom from 29 ppm to 31 ppm.

^{13}C NMR (121 MHz, T = 90 ^{o}C, Toluene-d_8, δ): 171.5 (C=O), 50.2 (**C**HCOOCO**C**H), 44.9 (**C**HCH$_2$**C**H, bridgehead), 42.0 (CH$_2$**C**H**C**HCH$_2$)**,** 37.0 (CH**C**H$_2$CH, bridge), 30.4-30.2 (**C**H$_2$), 30.1 (s-EN<u>E</u>NE), 29.7 (CH$_2$**C**H$_2$CHCH**C**H$_2$CH$_2$), 29.5 (**C**H$_2$CH$_2$CHCHCH$_2$**C**H$_2$);

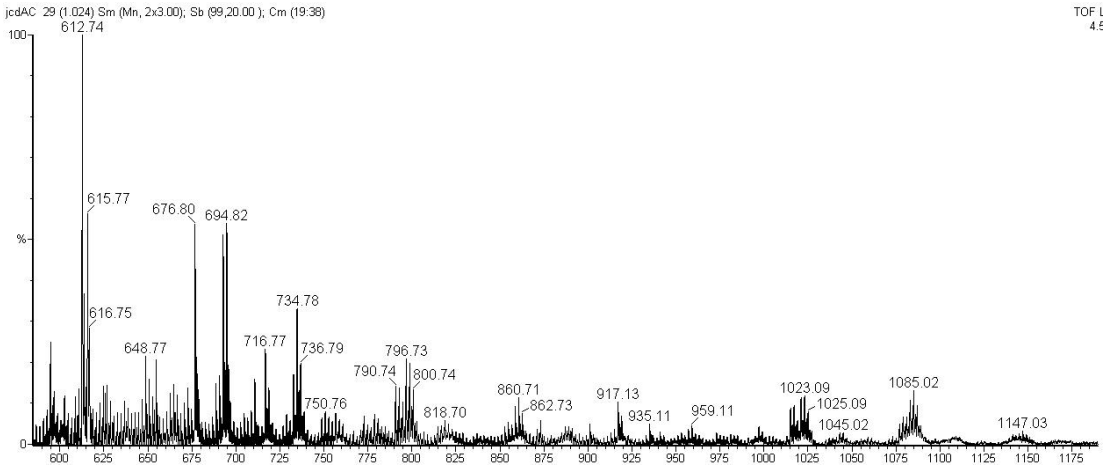


Figure 3b Maldi TOF of the copolymer of CA and ethylene. Matrix peaks appear below 750 m/z (for attribution, see Figure 1 of the main paper).

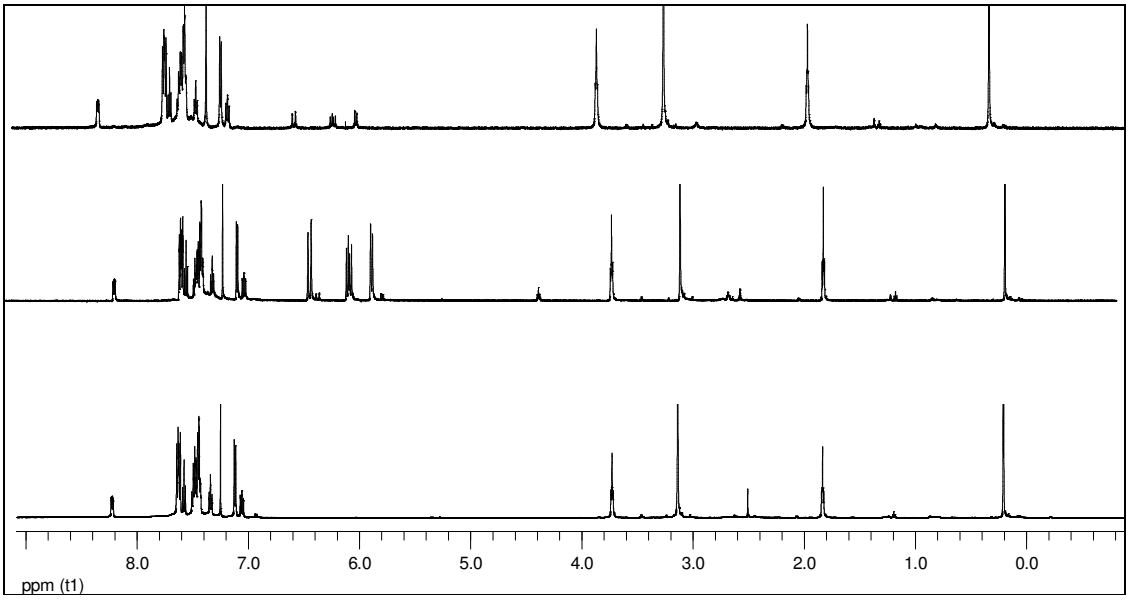


Figure 4. Heating catalyst **1b** (c = 90 mmol/L) in $CDCl_3$ in the presence of 2 equivalents of AA. Bottom spectrum : **1b** alone – Central spectrum : 1b + AA – Top : **1b** + AA after 8 hours heating at 50°C. Part of the AA has polymerized (insoluble white salt) via a thermally triggered radical mechanism (no inhibitor present). As a result, olefinic resonances (5.5 – 6.5 ppm) have disappeared. All catalysts resonances remain unchanged during this process.