

# Supporting Information

## Insertion Copolymerization of Difunctional Polar Vinyl Monomer with Ethylene

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## 1. General methods and materials:

Unless noted otherwise, all manipulations were carried out under an inert atmosphere using standard Schlenk line techniques or m-Braun glove box. Toluene was distilled from sodium, diethyl ether and THF from sodium/benzophenone under argon atmosphere. Acetonitrile and methylene chloride were distilled on calcium-hydride. Ethylene (99.995%; 5 grade) was supplied by Ms. Vadilal Chemicals Ltd, Pune, India. Acrylonitrile and Trifluoromethyl acrylic acid was supplied by Alfa-Aesar. Ethyl-2-cynoacrylate was supplied by sigma-aldrich and was used as received. Methylacrylate was supplied by sigma-aldrich, which was distilled from 4.5 Å linde molecular sieves before use.  $[(\text{COD})\text{PdMeCl}]^1$ ,  $[2-(2\text{-methoxyphenyl})\text{phosphino}]\text{benzenesulphonic acid}^2$ , Acetone-dimer  $[\{(1\text{-Cl})\text{-}\mu\text{-Na}\}_2]^3$  (**2**) were synthesized following known procedures. The copolymerization was run in a Buechi glas uster cyclone 075 high pressure reactor equipped with overhead mechanical stirrer, heating/cooling jacket and pressure regulators.

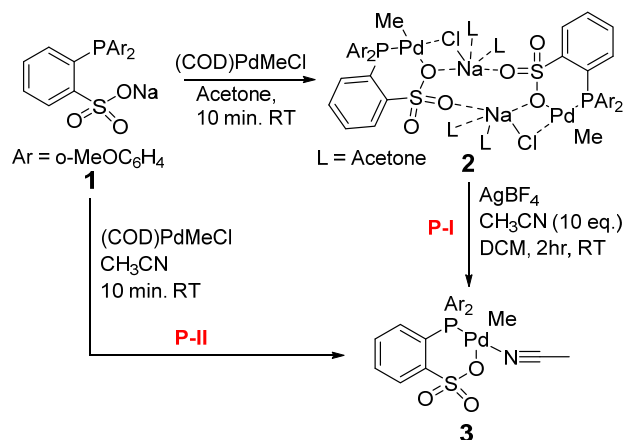
Solution NMR spectra were recorded on a Bruker Avance 200, 400, 500 and 700 MHz instruments. Chemical shifts are referenced to external reference TMS ( $^1\text{H}$  and  $^{13}\text{C}$ ) or 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ). Coupling constants are given as absolute values. Multiplicities are given as follows s: singlet, d: doublet, t: triplet, m: multiplet. High temperature NMR of the copolymers was recorded in  $\text{C}_2\text{D}_2\text{Cl}_4$  solution at  $130^\circ\text{C}$  or  $\text{C}_6\text{D}_6+\text{TCB}$  (10:90) mixture at  $120^\circ\text{C}$ . FT-IR spectra were recorded on a Bruker  $\alpha\text{-T}$  spectrophotometer in the range of  $4000\text{-}400\text{ cm}^{-1}$ . Mass spectra were recorded on Thermo scientific Q-Exactive mass spectrometer, the column specification is Hypersil gold C18 column  $150 \times 4.6\text{ mm}$  diameter  $8\text{ }\mu\text{m}$  particle size mobile phase used is 90% methanol + 10 % water + 0.1 % formic acid. Differential scanning calorimeter (DSC) was carried out on DSC Q-10 from TA instruments at a heating and cooling rate of  $10\text{ K min}^{-1}$ . High-temperature Gel Permeation Chromatography (HT-GPC) of the polymers was recorded in 1,2,4-trichlorobenzene at  $160^\circ\text{C}$  on a Viscotek GPC (HT-GPC module 350A) instrument equipped with triple detector system. The columns were calibrated with linear polystyrene standards and the reported molecular weights are with respect to polystyrene standards. MALDI-ToF-MS was performed on AB SCIEX TOF/TOF  $^{\text{TM}}$  5800 and Dithranol was used as a matrix.

## 2. Complex synthesis:

### 2.1 Synthesis of Pd-phosphinesulfonate-acetonitrile complex 3: Route P-I:

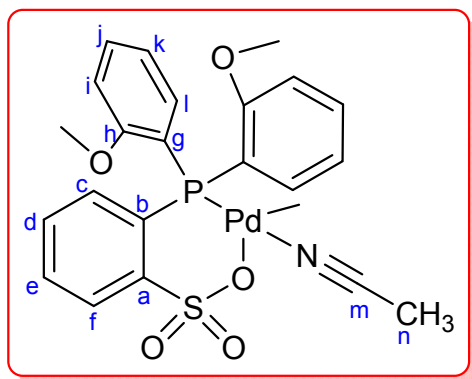
Synthesis of acetone-dimer **2** is reported; following which complex **2** (78%) was prepared in good yields.<sup>3</sup> 65 mg (0.05 mmol) of **2**, 20.4 mg (0.105 mmol, 2.05 equiv) of  $\text{AgBF}_4$  was weighed in glove-box and was transferred to a Schlenk tube with magnetic needle. To this mixture 0.4 ml (10 mmol, 200 equiv.) of acetonitrile was added followed by 10 ml of dichloromethane. The

reaction mixture was stirred for 2 hours in dark, after which the soluble fraction was cannula filtered into 50 ml Schlenk flask to give yellow colored solution. The Schlenk tube was washed with 5 ml of DCM and the soluble fraction was cannula filtered. The combined filtrate was evaporated very slowly under reduced pressure to afford yellow crystals which were characterized by single crystal XRD.



## 2.2 Direct synthesis of Pd-phosphinesulfonate-acetonitrile complex 3: Route P-II

The sodium-salt of phosphinesulfonate ligand **1** (75.1 mg, 0.17 mmol) was mixed with cyclooctadiene-palladium-methylchloride (50 mg, 0.165 mmol, 1 equivalent) in Schlenk tube.



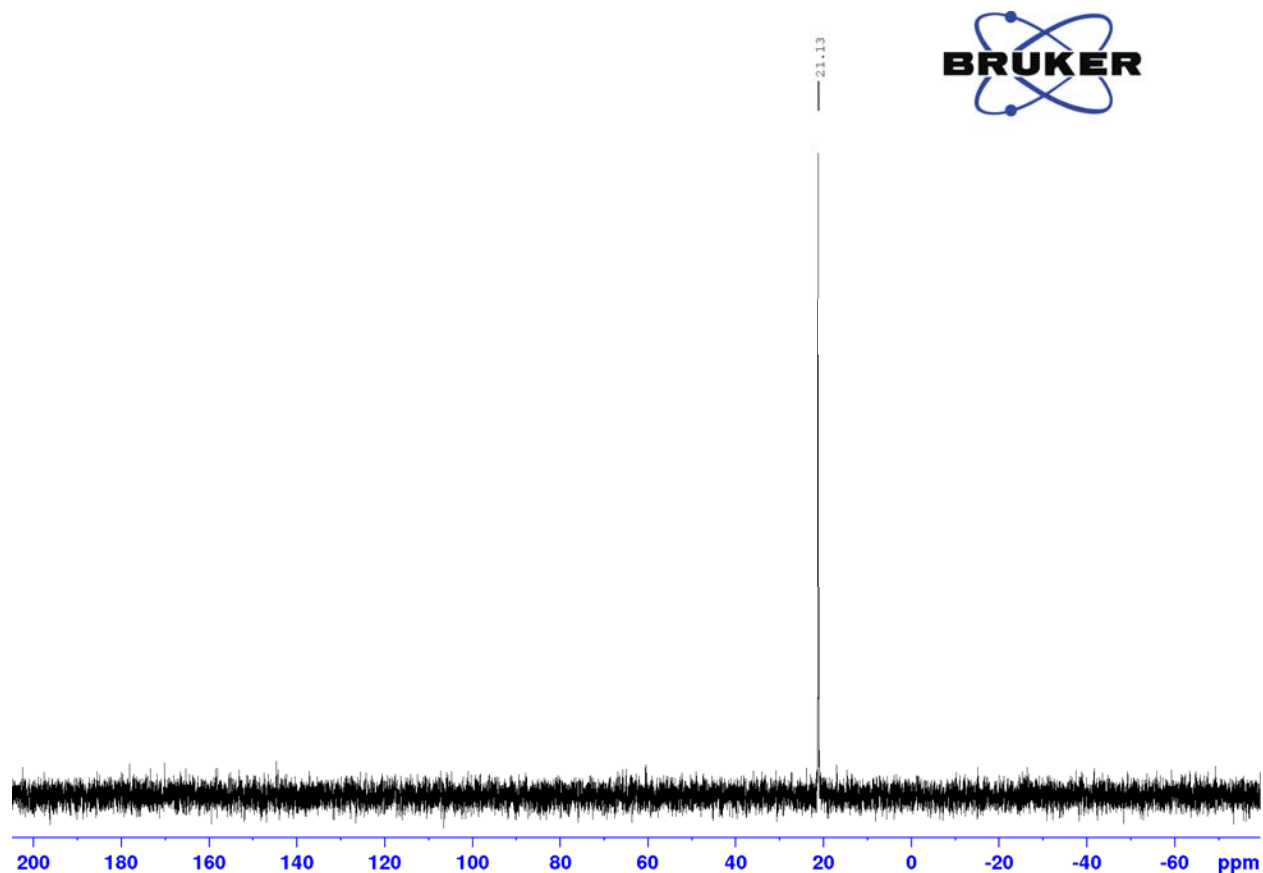
Acetonitrile (30 ml) was added to this Schlenk tube and the reaction mixture was stirred for 5 minutes leading to a clear solution. The clear solution was cannula filtered and the filtrate was passed through celite bed. The celite was washed with 10 ml of acetonitrile (3 × 10 ml) and the filtrate was collected in Schlenk flask. The volatiles were evaporated in vacuum and the yellowish white powder was washed with diethyl ether (10 ml). The residue was dried for 3 hours in vacuum to produce complex **3** as yellowish white powder (88 mg, 0.15 mmol) in 91% yield. The spectroscopic and analytical

data is exactly same as complex **3** obtained via route P-I.

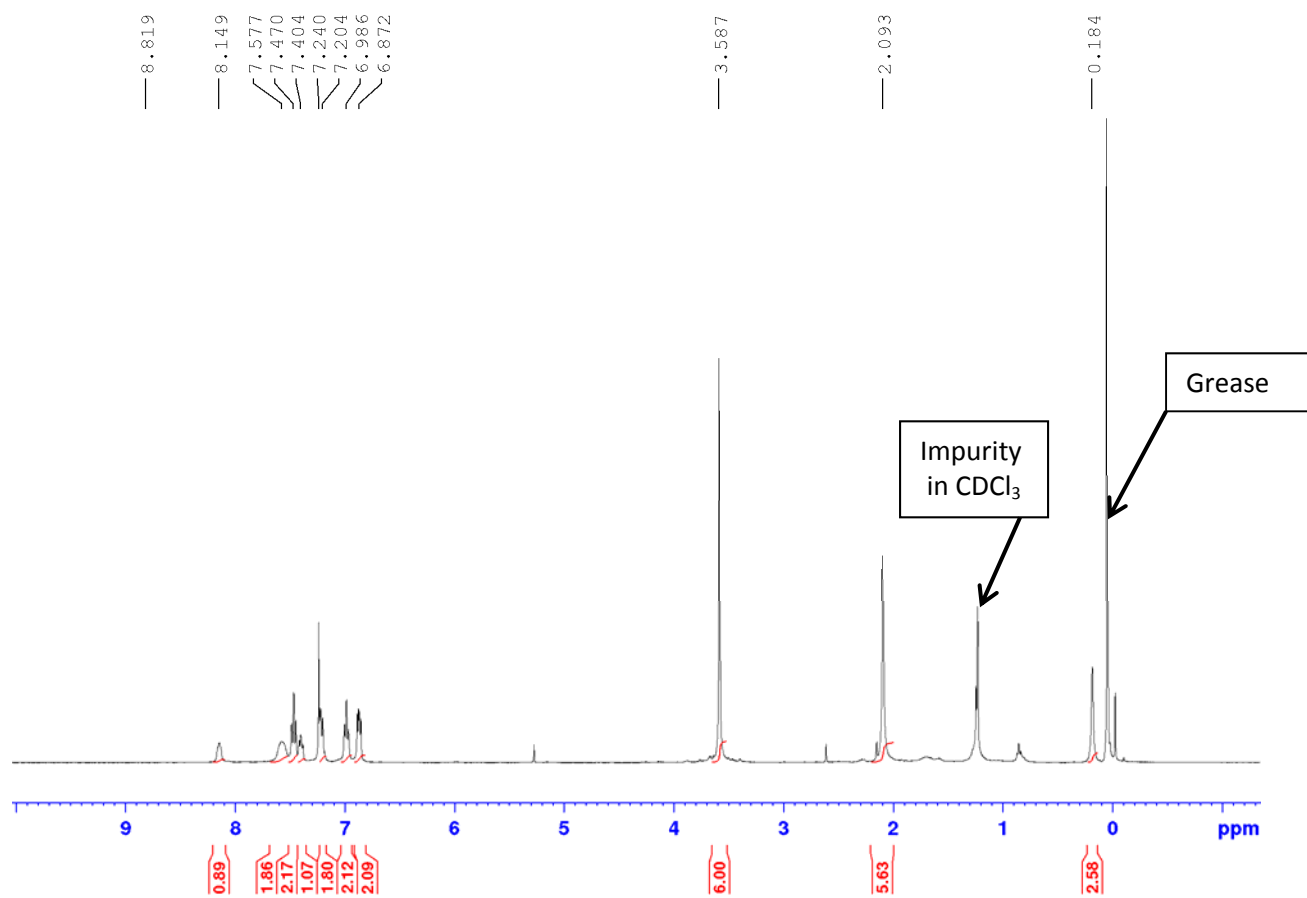
The complex was also characterized using single crystal X-ray diffraction as depicted in figure S7.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K):** δ = 8.15 (s, 1H), 7.58 (bs, 2H), 7.47 (t, <sup>3</sup>J<sub>H-H</sub> = 7.53 Hz, 2H), 7.40 (m, 1H), 7.20 (m, 2H), 6.98 (t, <sup>3</sup>J<sub>H-H</sub> = 7.37 Hz, 2H), 6.87 (dd, J<sub>H-H</sub> = 3.3 Hz, 4.6 Hz, 2H), 3.59 (s, 6H), 2.09 (s, 6H), 0.18 (s, 3H, Pd-Me). **<sup>31</sup>P NMR (500 MHz, CDCl<sub>3</sub>, 298 K):** δ = 21.1. **<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, 298 K):** δ = 160.6 (s, C<sub>h</sub>), 148.3 (br, s, C<sub>a</sub>), 137.9 (br, s, C<sub>e</sub>), 134.5 (s, C<sub>c</sub>), 133.5 (s, C<sub>j</sub>), 130.3 (s, C<sub>i</sub>), 128.4 (d, J<sub>PC</sub> = 7.17, C<sub>d</sub>), 128.01 (d, J<sub>PC</sub> = 7.97, C<sub>f</sub>), 127.7 (d, <sup>1</sup>J<sub>PC</sub>

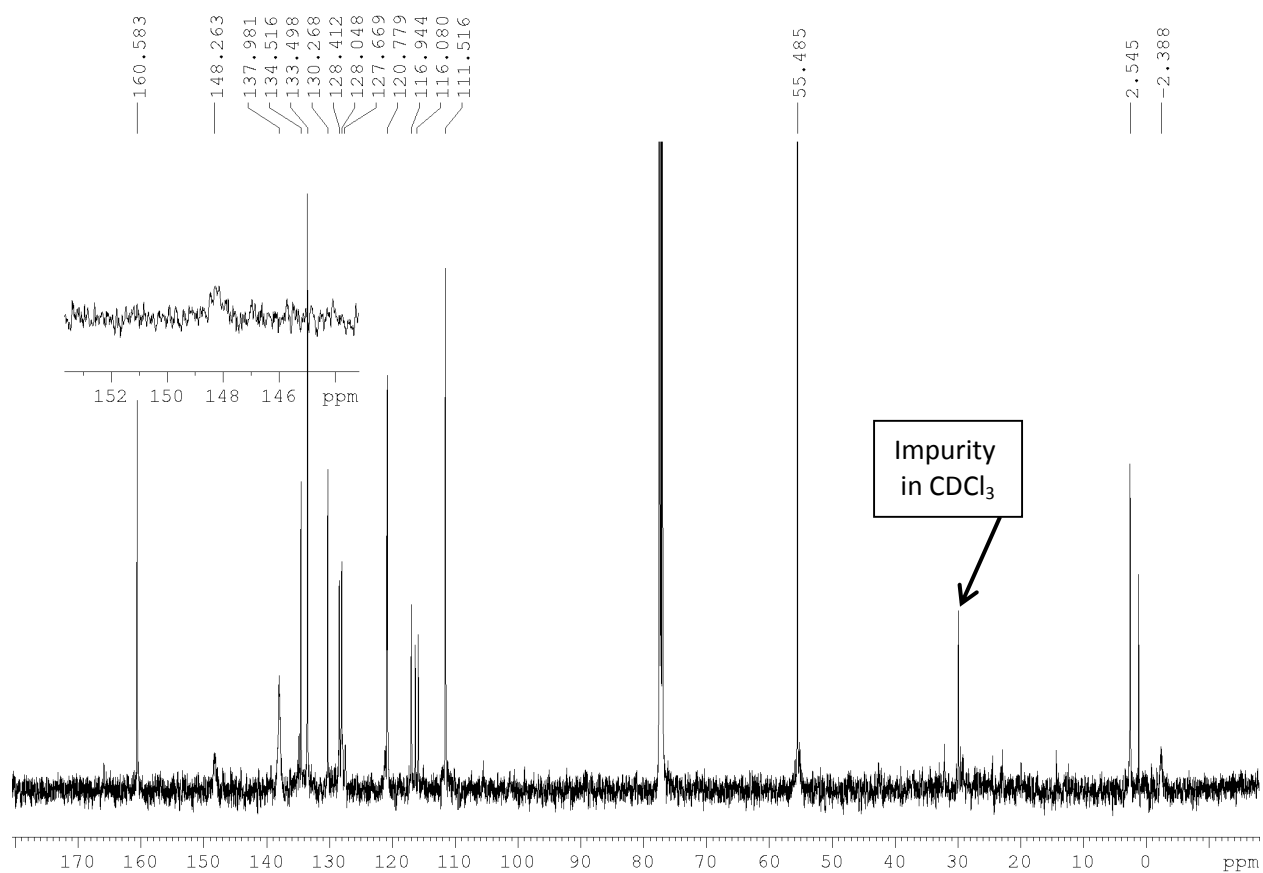
= 51.77, C<sub>b</sub>), 120.8 (d,  $J_{PC} = 12.05$ , C<sub>k</sub>), 116.9 (s, C<sub>m</sub>), 116.08 (d,  $^1J_{PC} = 59.03$ , C<sub>g</sub>), 111.2 (d,  $J_{PC} = 4.1$ , C<sub>i</sub>), 55.5 (s, OCH<sub>3</sub>), 2.5 (s, C<sub>n</sub>), -2.4 (br, s, Pd-CH<sub>3</sub>). ESI-MS (+ve) m/z = 544.97 [M-ACN+Na]<sup>+</sup>



**Figure S1:** <sup>31</sup>P NMR spectrum of complex **3** in CDCl<sub>3</sub> (500 MHz, 298K).

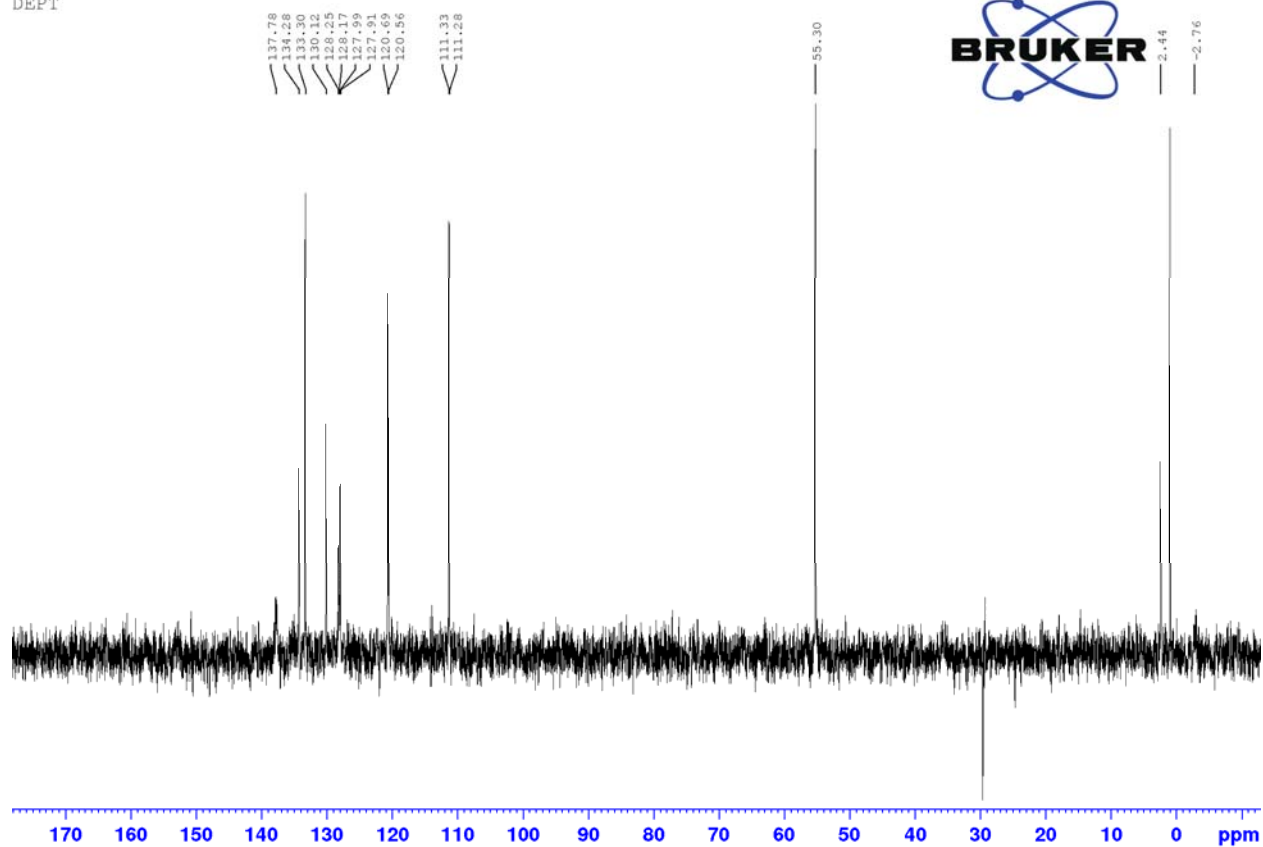


**Figure S2:**  $^1\text{H}$  NMR spectrum of complex **3** in  $\text{CDCl}_3$  (500 MHz, 298K).

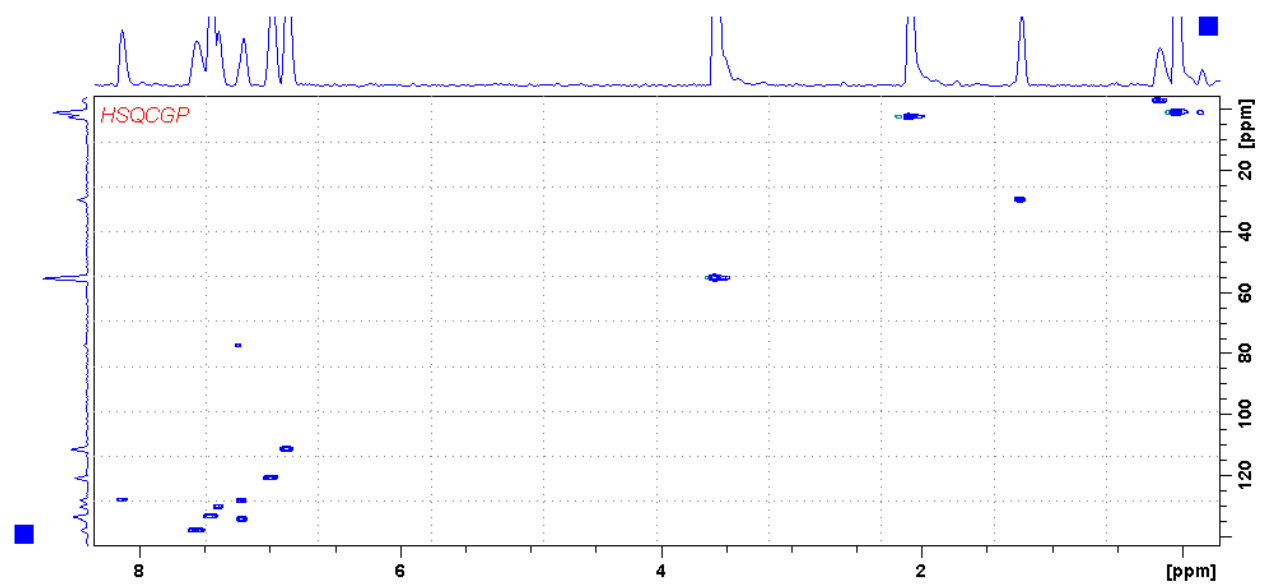


**Figure S3:**  $^{13}\text{C}$  NMR spectrum of complex **3** in  $\text{CDCl}_3$  (400 MHz, 298K).

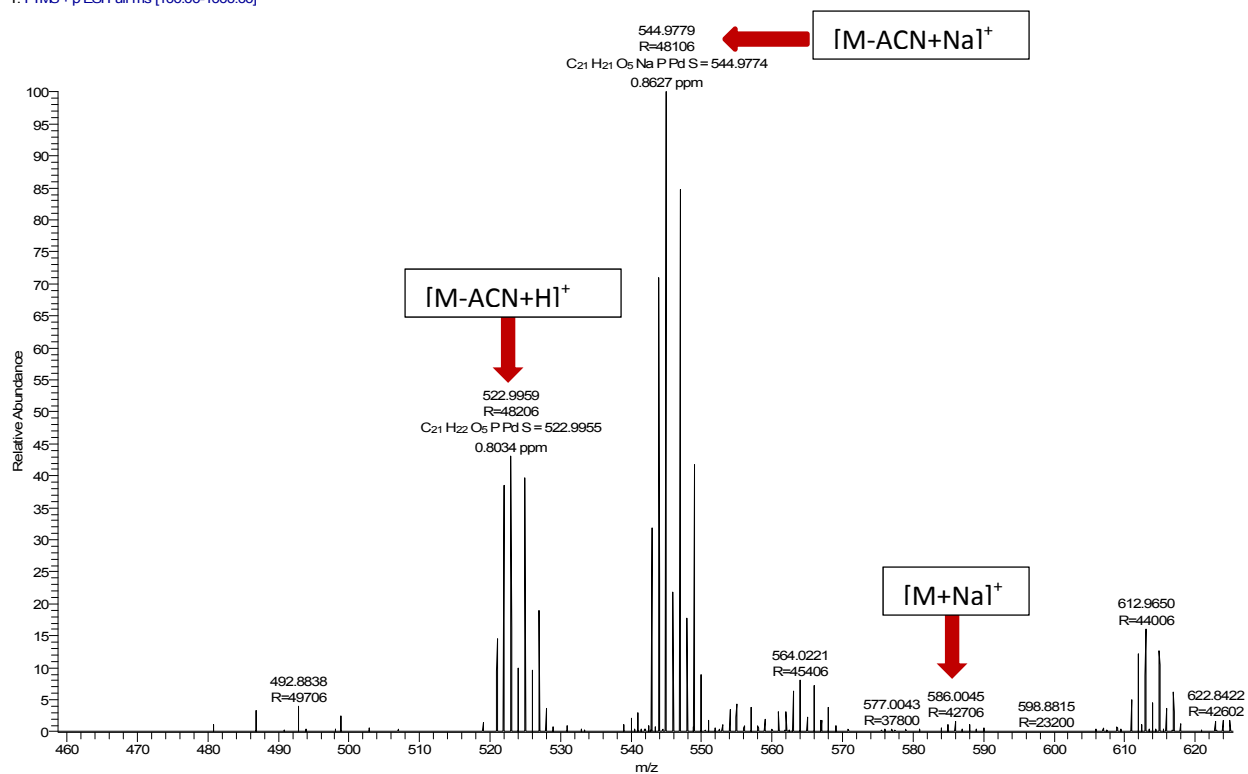
DEPT



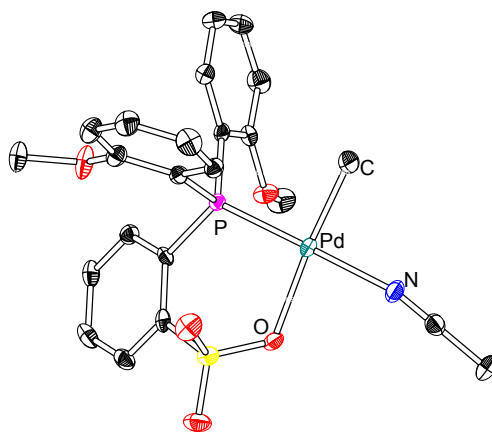
**Figure S4:** 135-DEPT spectrum of complex **3** in  $\text{CDCl}_3$  (400 MHz, 298K).



**Figure S5:** HSQC NMR spectrum of complex **3** in  $\text{CDCl}_3$  (400 MHz, 298K).



**Figure S6:** ESI-MS (+Ve) spectrum of complex 3 ( $C_{23}H_{24}NO_5PPdS$ )  $m/z = 544.97$   $[M-ACN+Na]^+$ .



**Figure S7:** Molecular structure of complex 3; solvent molecules and H-atoms are omitted for clarity; thermal ellipsoids are drawn at 50% probability level.



### Crystal data and structural refinement

Formula sum	C <sub>25</sub> H <sub>27</sub> N <sub>2</sub> O <sub>5</sub> PPdS
Formula weight	604.93 g/mol
Crystal system	orthorhombic
Space-group	P b c a (61)
Cell parameters	a=16.3061(7) Å b=16.4145(7) Å c=19.0195(8) Å
Cell ratio	a/b=0.9934 b/c=0.8630 c/a=1.1664
Cell volume	5090.69(40) Å <sup>3</sup>
Z	8
Calc. density	1.57846 g/cm <sup>3</sup>
RAI1	0.0497
Wyckoff sequence	c62

### 2.3 Relative binding strength of acetonitrile and DMSO in complex 3<sup>4</sup>:

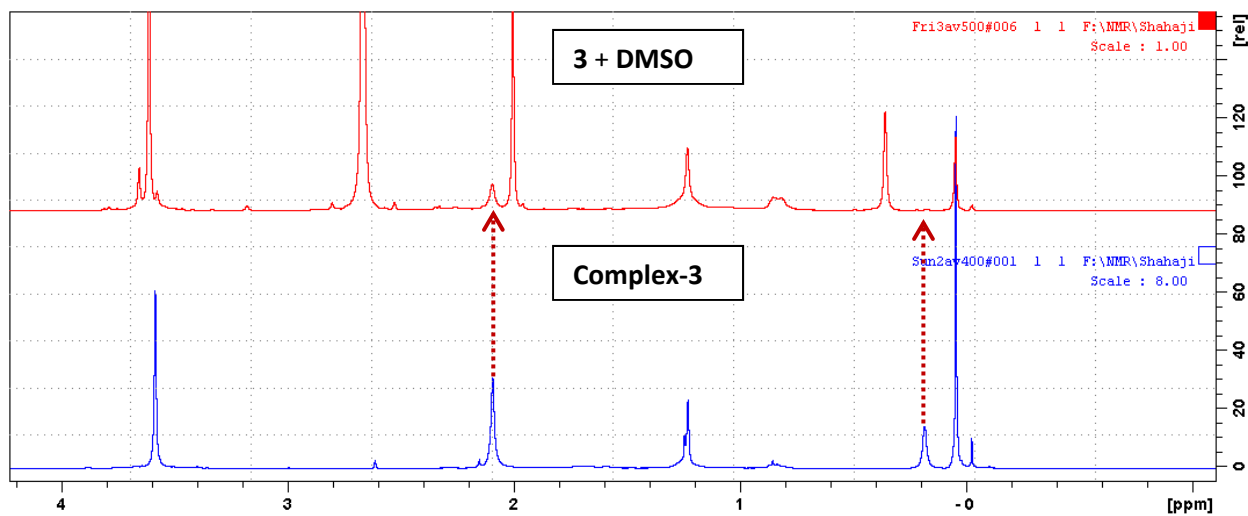
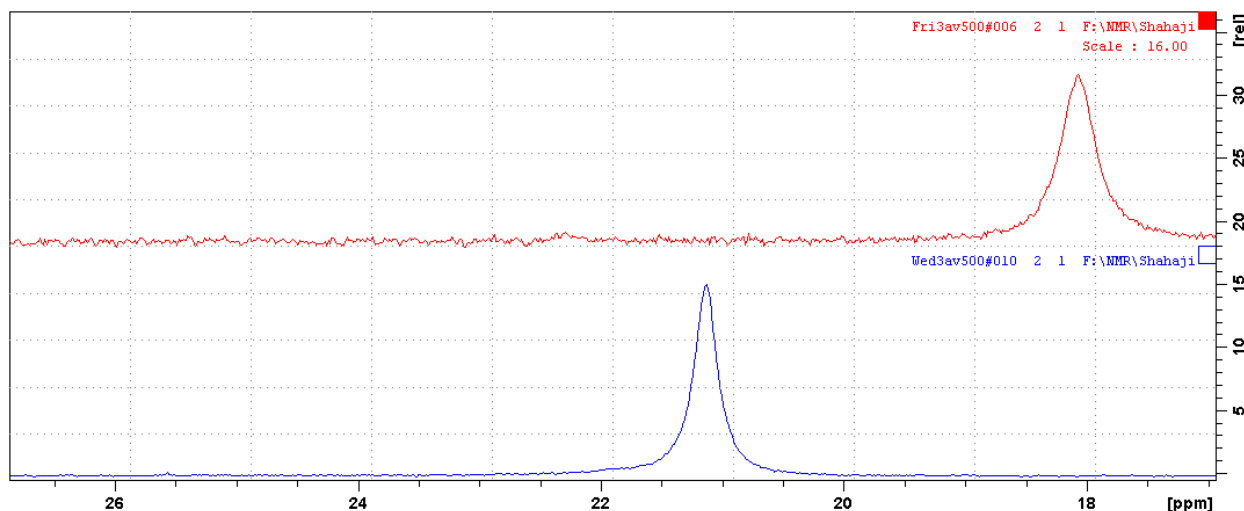


Figure S8: <sup>1</sup>H NMR of 3 (bottom) and displacement of acetonitrile from 3 by DMSO (top).



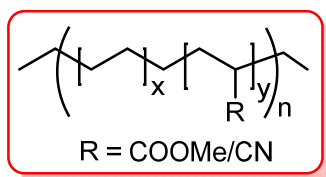
**Figure S9:**  $^{31}\text{P}$  NMR of **3** (bottom) and displacement of acetonitrile from **3** by DMSO (top).

**Table S1:** NMR data on relative binding strengths of DMSO and acetonitrile in complex **3**.

	Pd- $\text{CH}_3$	$\text{CH}_3\text{CN}$	DMSO	$^{31}\text{P}$
<b>3</b>	0.18	2.10	-	21.13
<b>3 + 1 eq. DMSO</b>	0.39	2.02	2.69	18.07

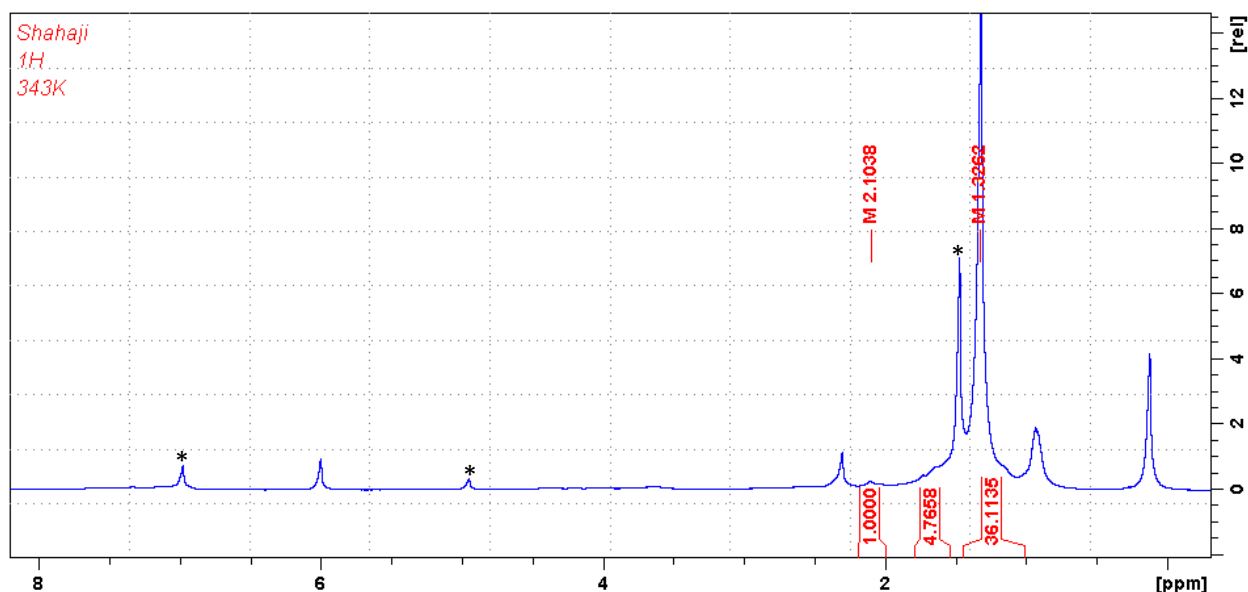
### 3. Copolymerization of ethylene-acrylonitrile/methyl acrylate:

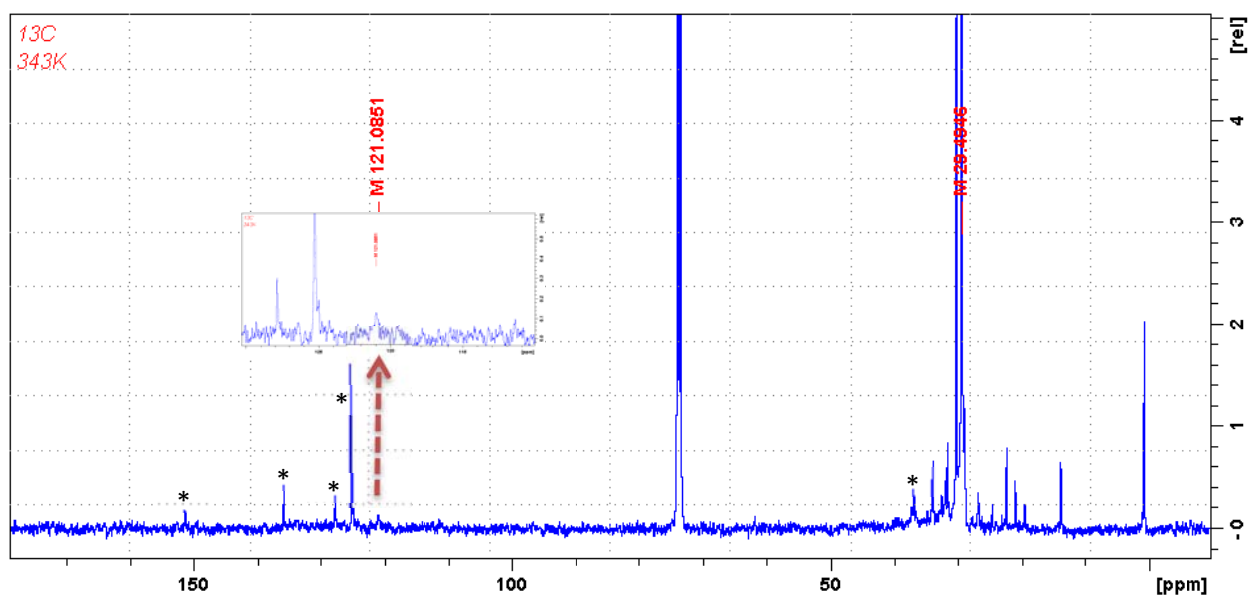
The ethylene- acrylonitrile/methylacrylate copolymerization was carried out in a 250 ml stainless steel high pressure reactor (Buechi) equipped with mechanical stirrer and heating/cooling jacket. Prior to the experiment, the reactor was heated in vacuum to 80°C for 30 minutes, cooled to room temperature and was filled with argon. Reactor was flushed with ethylene (3 times, 10 bars) and was charged with appropriate quantity of toluene under positive ethylene stream. Next, the reactor was pressurized to 5 bars and saturated with ethylene for 30 minutes at desired reaction temperature before it was cooled to room temperature. A solution of butylated hydroxyl toluene (37 mg, 0.16 mmol in 10 ml toluene), calculated amount of methylacrylate (diluted in 10 ml toluene) and catalyst solution (12 mg, 20  $\mu\text{mol}$  in 10 ml DCM) was introduced into the reactor at room temperature. The reactor was then pressurized to 5 bars with stirring and appropriate temperature (95°C) was reached within 1-5 minutes. The polymerization was generally carried out for 60 minutes, the excess ethylene was slowly vented off and the reactor was allowed to cool down to room temperature. The resultant solution was evaporated in vacuum to obtain solid mass, which was further dried under reduced pressure at 50°C for 8 hours or until constant



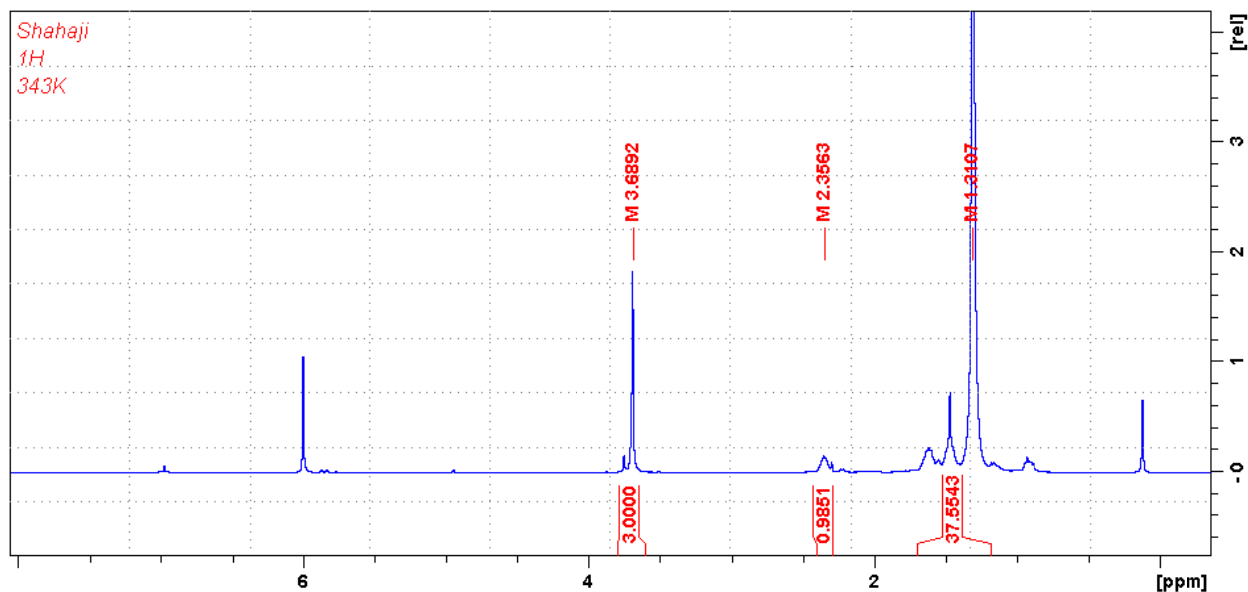
weight is obtained. The resultant copolymers were characterized using high temperature  $^1\text{H}$  NMR spectroscopy and methylacrylate/acrylonitrile incorporation was determined using the  $^1\text{H}$  NMR. Representative  $^1\text{H}$  NMR spectra of the copolymers are depicted in figures S10-14. The reactivity of catalyst **3** in copolymerization was tested and the results are summarized in table S2. The Pd-complex **3** catalyzes copolymerization of acrylonitrile and ethylene at  $95^\circ\text{C}$ . Insertion copolymerization of acrylonitrile and ethylene produced the desired copolymer with 9.2% acrylonitrile incorporation (table 1, run 1-1). Performance of **3** in another industrially important monomer, methyl acrylate, was tested. An incorporation of 9.6% was observed at 0.6 mol/lit. concentration and the polymer molecular weight was 3100 g/mol (run 1-2). Similar incorporation under identical conditions was observed with DMSO complex.<sup>7</sup>

Expt. No.	Catalyst conc.	Functional Olefin	FO Conc. (Mol/L it.)	Polymer Yield (g)	% Incorporation <sup>b</sup>	Mol.Wt. (Mn) <sup>c</sup>	PDI <sup>c</sup>
S2-1	20 μMol	AN	1.2	0.126	9.2	ND	ND
S2-2	20 μMol	MA	0.6	0.397	9.6	3100	1.3

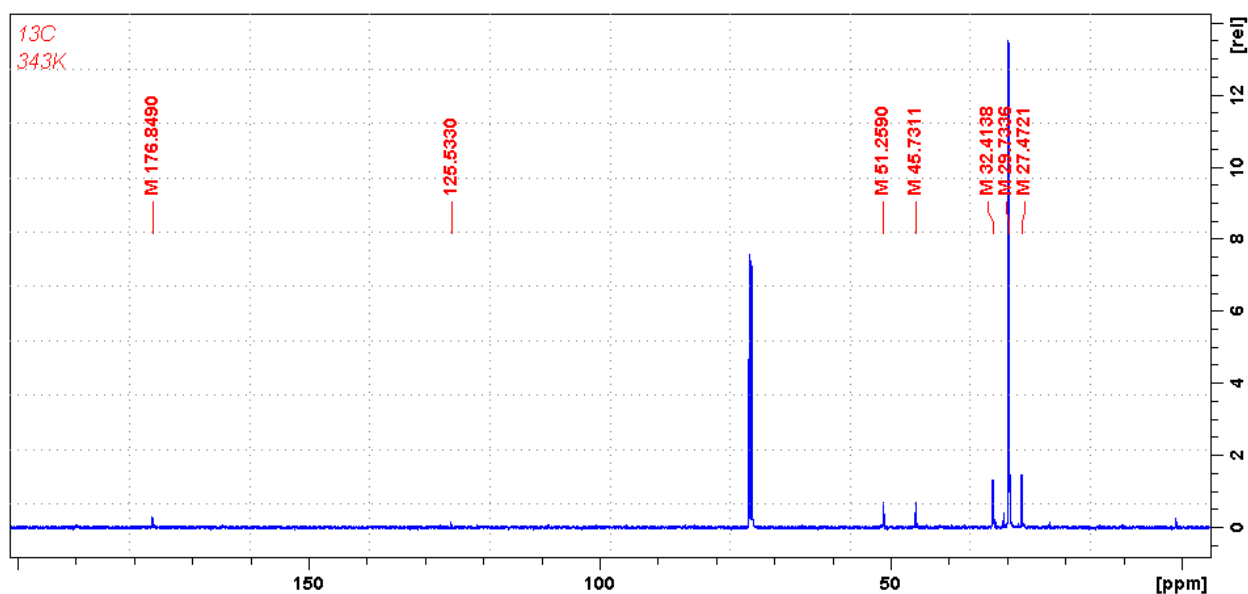




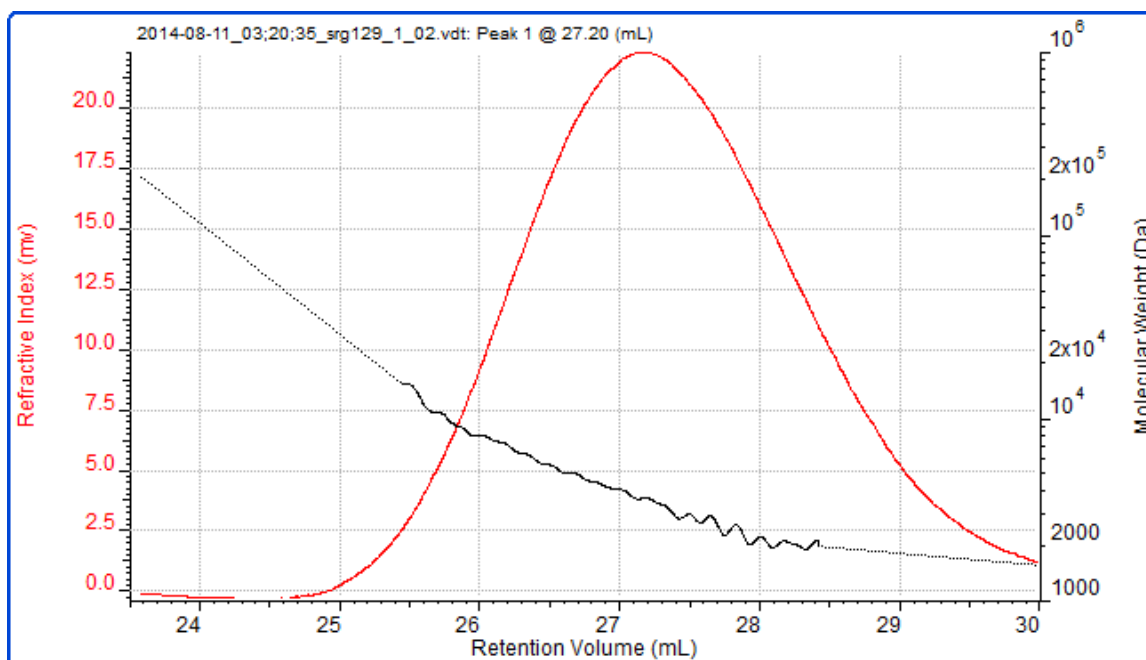
**Figure S11:** <sup>13</sup>C NMR of ET-AN copolymer in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 343K (TableS2, run-1); BHT signals are indicated with “\*” mark.



**Figure S12:** <sup>1</sup>H NMR of ET-MA copolymer in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 343K (TableS2, run-2).



**Figure S13:** <sup>13</sup>C NMR of ET-MA copolymer in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 343K (TableS2, run-2).



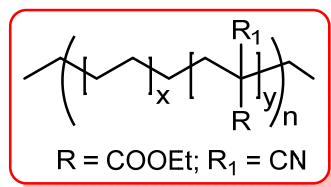
Data File: 2014-08-11\_03;20;35\_srg129\_1\_02.vdt Method: Aug2014-0003.vcm

Peak RV - (ml)	27.203
Mn - (Daltons)	3,080
Mw - (Daltons)	4,084
Mz - (Daltons)	6,253
Mp - (Daltons)	3,568
Mw / Mn	1.326

**Figure S14:** High temperature (HT)-GPC chromatogram of ET-MA copolymer in trichlorobenzene at 160°C (TableS2, run-2).

#### 4. Copolymerization of ethylene-ethyl-2-cynoacrylate:

The ethylene-ethyl-2-cyanoacrylate copolymerization was carried out in a 250 ml stainless steel high pressure reactor (Buechi) equipped with mechanical stirrer and heating/cooling jacket.



Prior to the experiment, the reactor was heated in vacuum to 80°C for 30 minutes, cooled to room temperature and was filled with argon. Reactor was flushed with ethylene (3 times, 10 bars) and was charged with appropriate quantity of toluene under positive ethylene stream. Next, the reactor was pressurized to appropriate ethylene pressure (1-10 bars) and saturated with ethylene for 30

minutes at desired reaction temperature before it was cooled to room temperature. A solution of butylated hydroxyl toluene (37 mg, 0.16 mmol in 10 ml toluene), calculated amount of ethyl-2-cyanoacrylate (diluted in 10 ml toluene) and catalyst solution (**3**: 12 mg, 20  $\mu\text{mol}$  in 10 ml DCM) was introduced into the reactor at room temperature. The reactor was then pressurized to desired ethylene pressure (1-10 bars) with stirring and appropriate temperature (95°C) was reached within 1-5 minutes. The polymerization was generally carried out for 60 minutes, the excess ethylene was slowly vented off and the reactor was allowed to cool down to room temperature under argon. The resultant solution was transferred to a Schlenk flask with syringe and the volatiles were evaporated in vacuum to obtain solid mass. The thus obtained solid material was washed thrice with chloroform and the insoluble solid was dried under reduced pressure at 50°C for 8 hours or until constant weight is obtained. The insoluble copolymer fraction was thoroughly investigated using a combination of spectroscopic and analytical tools and the results are summarized in table S3.

**Table S3:** Copolymerization of ethylene–ethyl-2-cynoacrylate in presence of complex **3**<sup>a</sup>

Run	ECA(m ol/L)	C <sub>2</sub> H <sub>4</sub> (bar)	% Incorp. <sub>b</sub>	Yield (g)	Mn (10 <sup>3</sup> g/mol) <sup>c</sup>	Mw/M n <sup>c</sup>	TOF (C <sub>2</sub> H <sub>4</sub> )/mol(Pd)/h	Tm°C
S3-1	0.03	5	0.32	0.90	4.7	1.5	1.60	129.2
S3-2	0.06	5	2.09	0.79	8.2	1.4	1.30	128.8
S3-3	0.12	5	4.92	0.87	6.4	1.7	1.55	130.0
S3-4	0.06	1	6.51	0.20	5.8	1.6	0.36	123.6
S3-5	0.06	10	1.9	1.09	8.3	1.4	1.96	129.7
S3-6 <sup>d</sup>	0.06	1	2.01	0.21	4.9	1.2	0.36	ND
S3-7 <sup>e</sup>	0.06	1	ND	0.19	ND	ND	0.33	ND

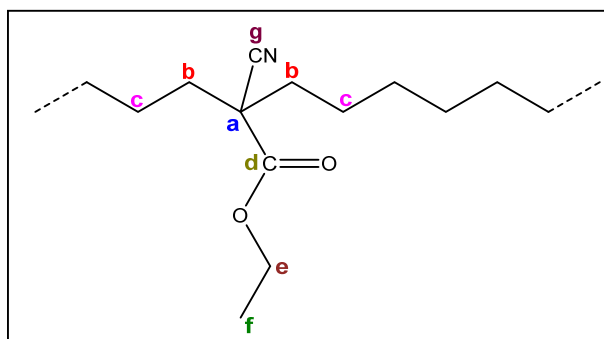
<sup>a</sup>Reaction conditions: **3** = 20 μmol in DCM, toluene = 50 ml (Toluene + ECA); temperature = 95°C, time = 1 hour,

<sup>b</sup>ECA incorporation was determined by high temperature <sup>1</sup>H NMR in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 130°C; <sup>c</sup>Determined by high temperature GPC at 160°C in tri-chlorobenzene against PS standard; <sup>d</sup>20 μmol of DMSO complex of type **3** was used as catalyst; <sup>e</sup>Galvinoxyl (0.2 mmol) was used as radical inhibitor; ND = Not determined.

## 5. Copolymer analysis:

### 5.1 <sup>1</sup>H NMR of copolymers and determination of functional olefin incorporation:

The ethylene functional olefin copolymerization experiments were performed at different



functional olefin concentration to establish the exact chemical shifts of the protons originating from the incorporated functional olefin. The proton chemical shifts were further corroborated by <sup>13</sup>C NMR chemical shifts. The resultant copolymers were insoluble in most of the common solvents at room temperature; hence a high temperature NMR was recorded. As a representative example, we choose run S3-4 (table S3) and

the proton NMR (as well as <sup>13</sup>C NMR) of the resultant polymer is described as under (see fig. S15).

**<sup>1</sup>H NMR (500 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 403 K):** δ = 4.46 (br., s, H<sub>e</sub>), 2.89-2.30 (br., m, H<sub>b</sub>), 1.49 (br., s, H<sub>f</sub>), 1.38 (br., s, H<sub>c</sub>). **<sup>13</sup>C NMR (500 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 403 K):** δ = 165.1 (C<sub>d</sub>), 117.3-113.7 (C<sub>g</sub>), 64.6 (C<sub>e</sub>), 45.7-43.2 (C<sub>a</sub>, C<sub>b</sub>), 29.4 (C<sub>c</sub>), 13.6-12.9 (C<sub>f</sub>).

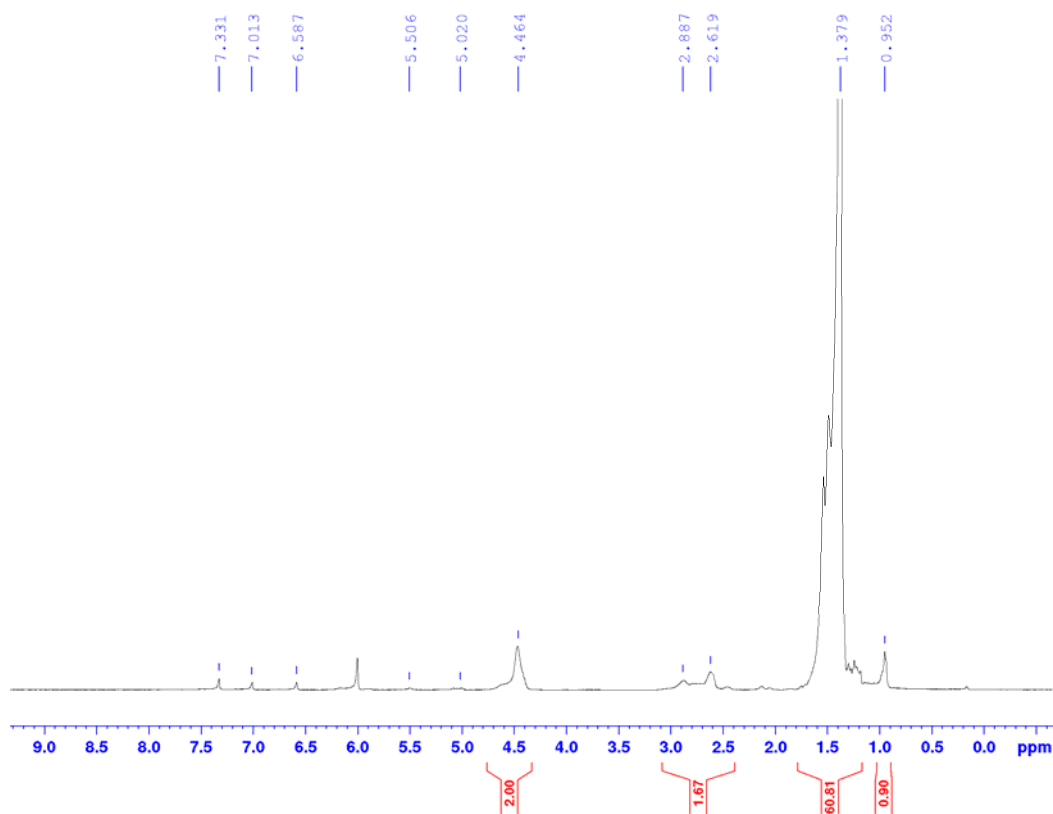
The copolymer composition was determined by high temperature proton NMR spectroscopy. An exemplary percent functional olefin incorporation is presented for the run with highest incorporation (table S3 run S3-4). The –OCH<sub>2</sub> (at 4.46 ppm) resonance, calibrated at 2 protons, was taken as reference.<sup>5</sup> Figure S15 depicts the corresponding proton NMR with respective

integrals. Similar protocol was followed for the rest of the copolymers and the respective percent incorporation was determined.

$$\begin{aligned} \% \text{ Incorporation} &= \frac{100}{1 + \left[ \frac{(A-5)}{4} \right]} \\ &= 100 / \{1 + [60.81+1.67-5/4]\} \\ &= 100 / \{1 + [62.48-5/4]\} \\ &= 100 / \{1 + [57.48/4]\} \\ &= 100 / \{1 + 14.37\} \end{aligned}$$

**A** = Total proton integration between  $\delta$  1.0-4.5; except reference  
 5 = Total ECA protons except ref.  
 4 = Total ethylene protons.

$$\% \text{ Incorporation} = 6.5 \%$$

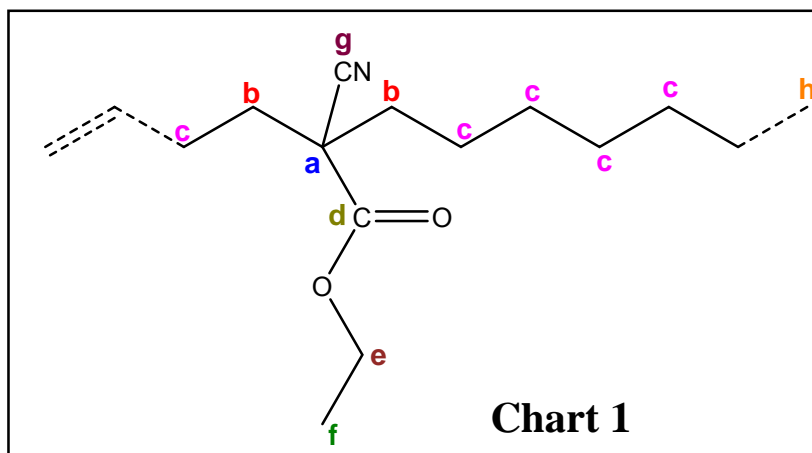


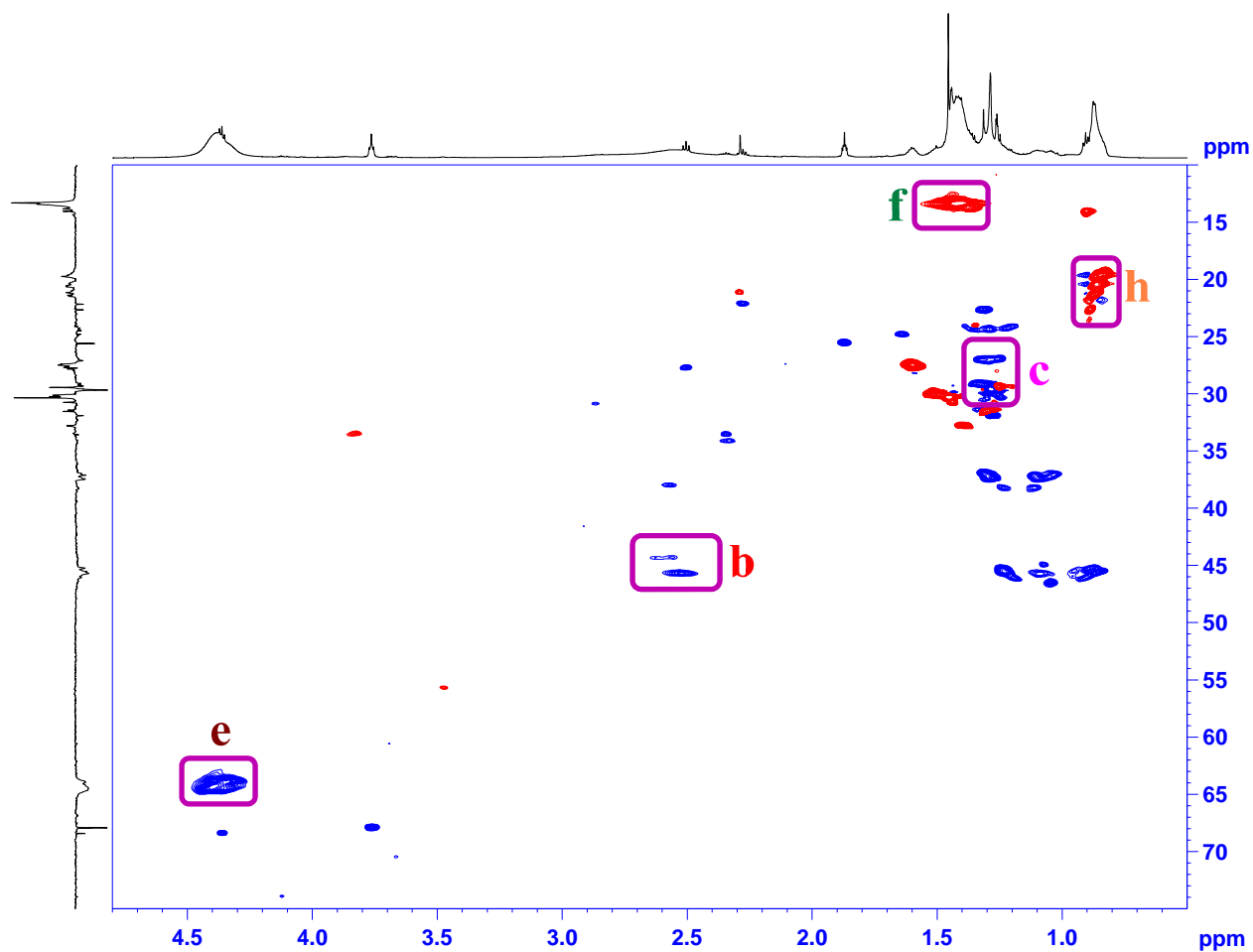
**Figure S15:**  $^1\text{H}$  NMR of ET-ECA copolymer in  $\text{C}_2\text{D}_2\text{Cl}_4$  at 403K (TableS3, S3-4)

## 5.2 Detection of ECA incorporation:



In our attempts to access the low molecular weight (chloroform soluble) copolymer fraction; the resultant copolymer after the polymerization reaction was dissolved in  $\text{CDCl}_3$ . Note that this sample consists of ECA homopolymer as well, which is otherwise washed-out with chloroform. Therefore, the 2D spectra displays many cross peaks, indicating different chemical environment around the  $-\text{CH}_2$  groups (originating from copolymer and the ECA homopolymer). In a direct ( $^1J_{\text{C-H}}$ ) C-H correlation HSQC spectrum, connectivity between b, c, e, f, h groups could be established (see figure S16A). However, crucial information on the connectivity between “a” type protons (see chart 1) and carbon, and “b” type protons and carbon was extracted from H-H and long range (HMBC) C-H correlation spectroscopy. In a  $^1\text{H}$  COSY experiment, a cross peak displaying a connectivity between “a” type protons to “b” type protons (see chart 1) could be detected (figure S16B). Similarly, HMBC displayed cross peaks that established connectivity between “a” type protons to “a” carbons; “a” protons to “b” type carbon and vice-versa (see figures S16C-D). A comparison between a  $^1\text{H}$  COSY spectrum of ET-ECA copolymer and ECA-homopolymer reveals a cross peak between “a” type protons with “b” type protons; clearly establishing the incorporation of ECA in ethylene chain (see figure S16E). Additionally, the incorporation was further corroborated by MALDI-ToF-MS findings (see table S4) and representative MALDI-ToF-MS spectra (run S3-3) are depicted in figures S17A-E. Various copolymer fractions have been identified and table S4 summarizes molar mass along with composition.





**Figure S16A:** Edited HSQC NMR of ET-ECA copolymer at 318K in  $\text{CDCl}_3$ . In the edited HSQC experiment,  $\text{CH}_2$  carbons appear with a negative phase (blue) while the  $\text{CH}$  and  $\text{CH}_3$  carbons appear with positive (red) phase. The DEPT-135 spectrum is plotted along the Y-axis.

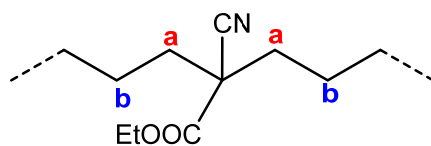


Chart 1

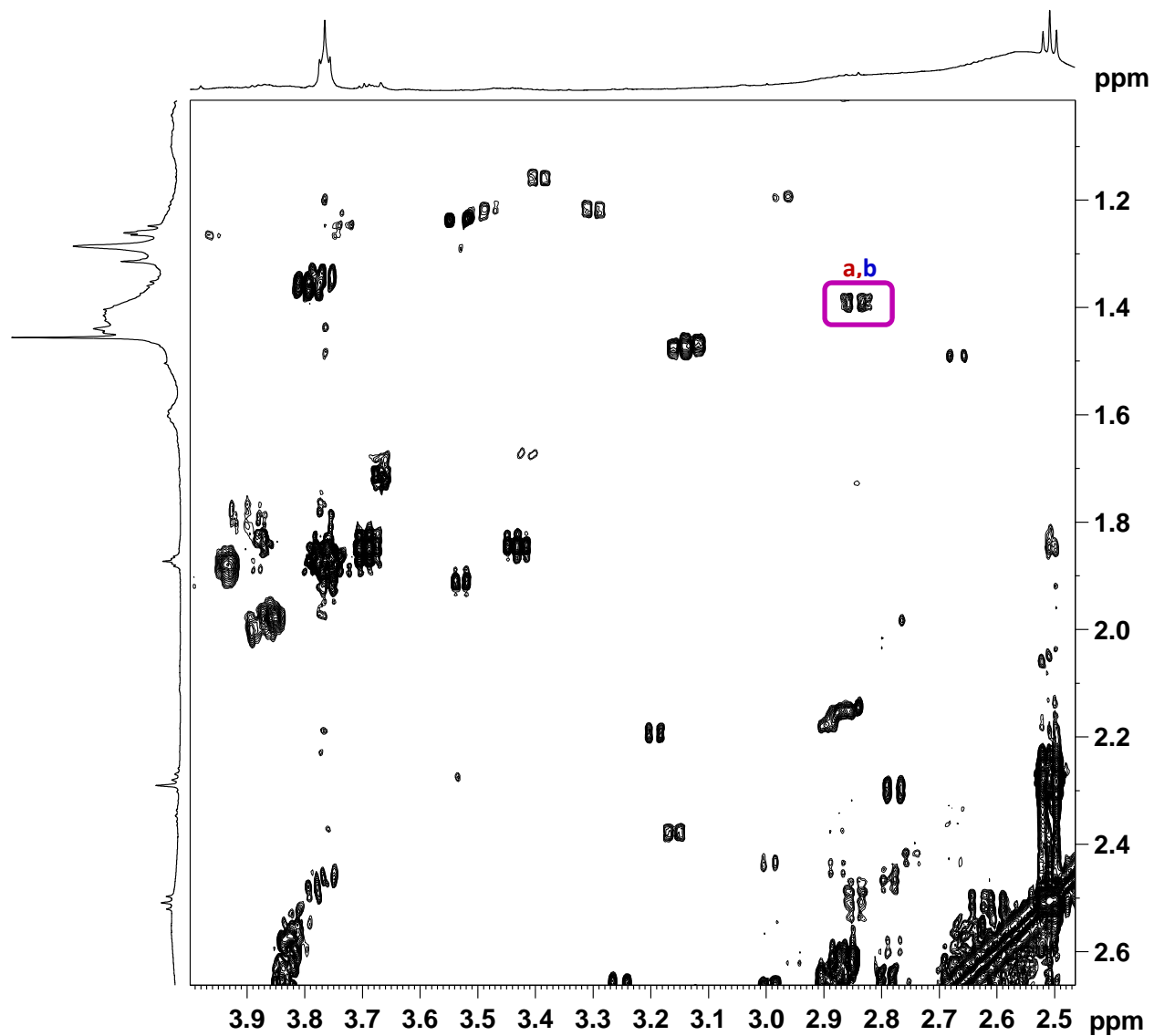
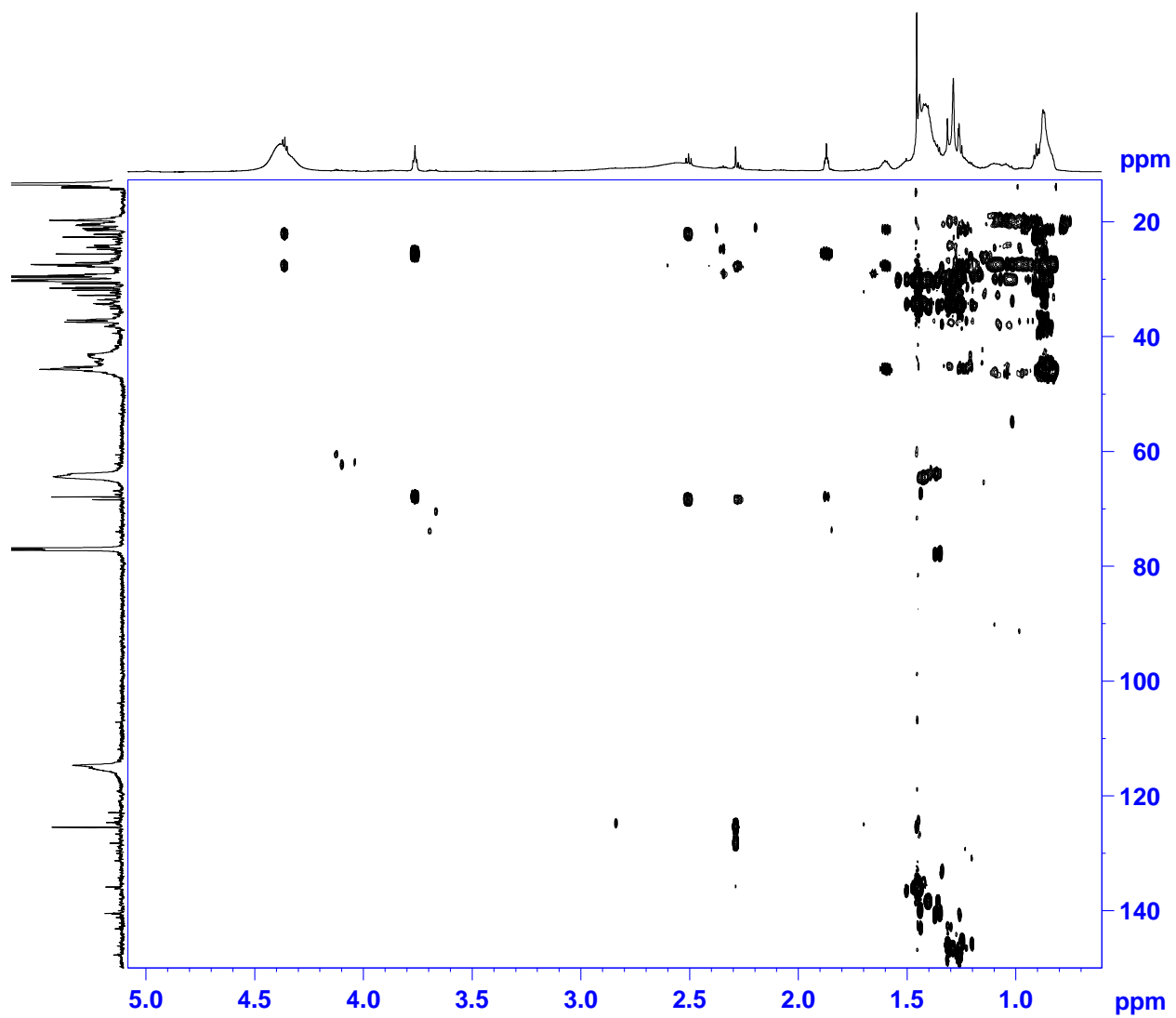
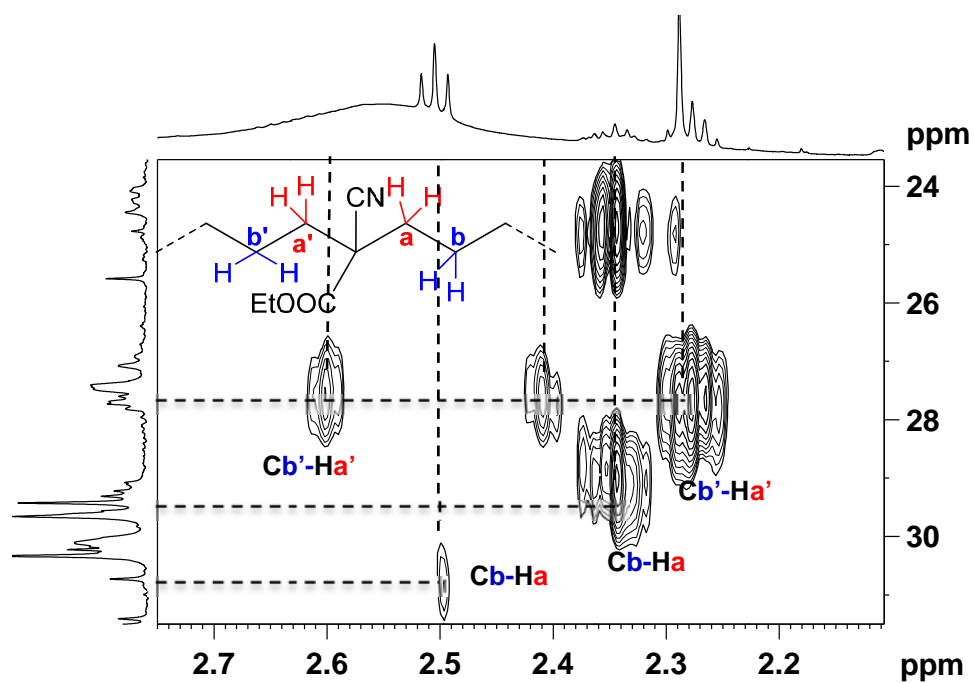


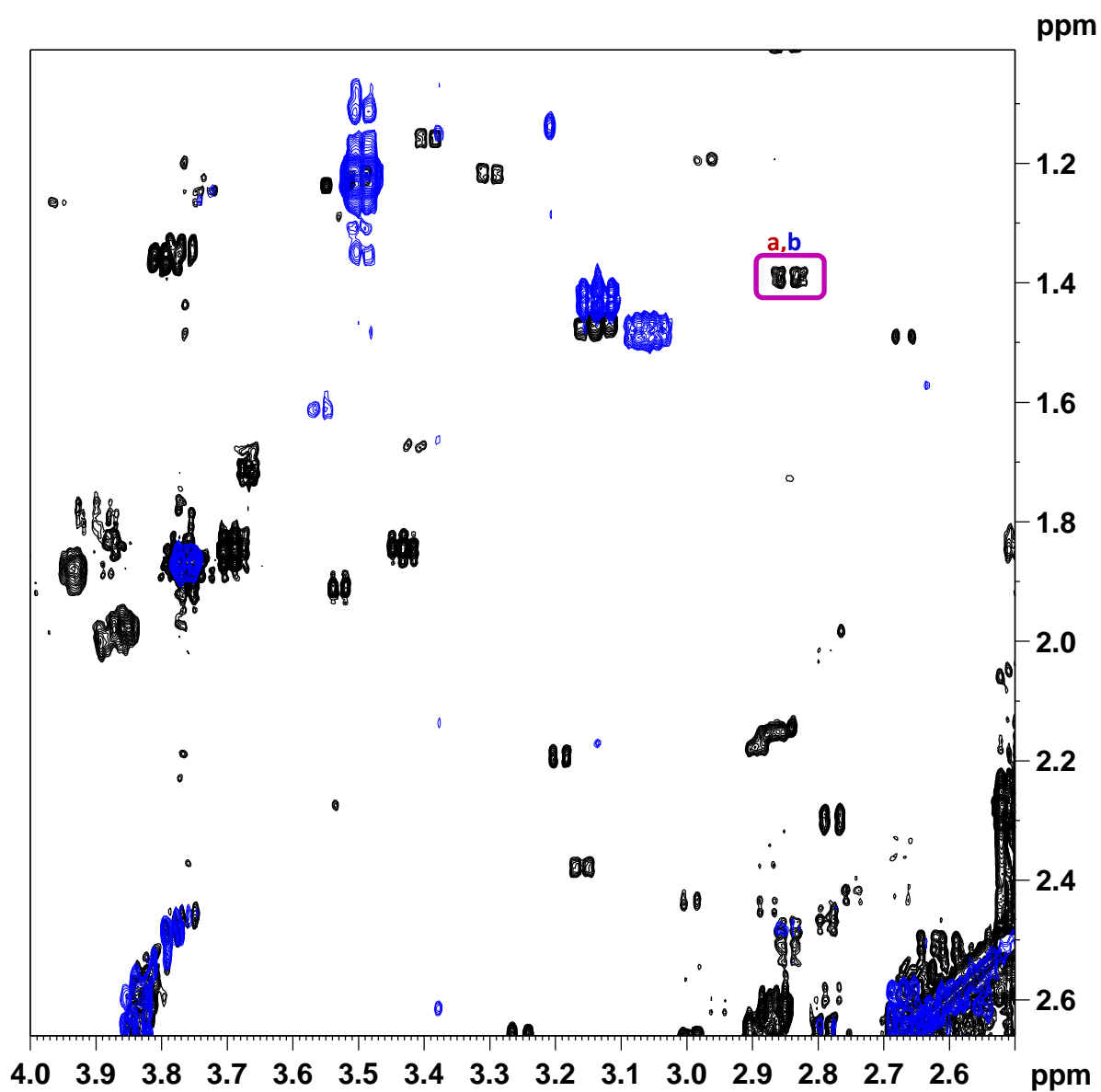
Figure S16B:  $^1\text{H}$  COSY NMR of ET-ECA copolymer at 318K in  $\text{CDCl}_3$ .



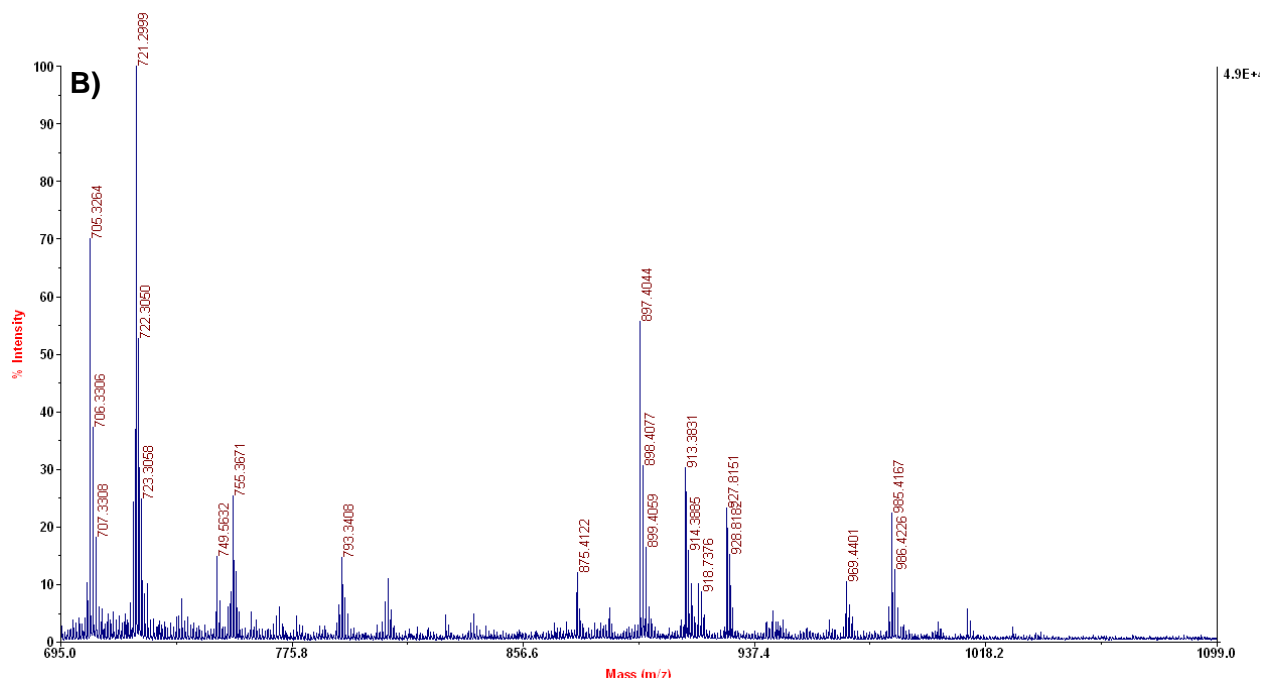
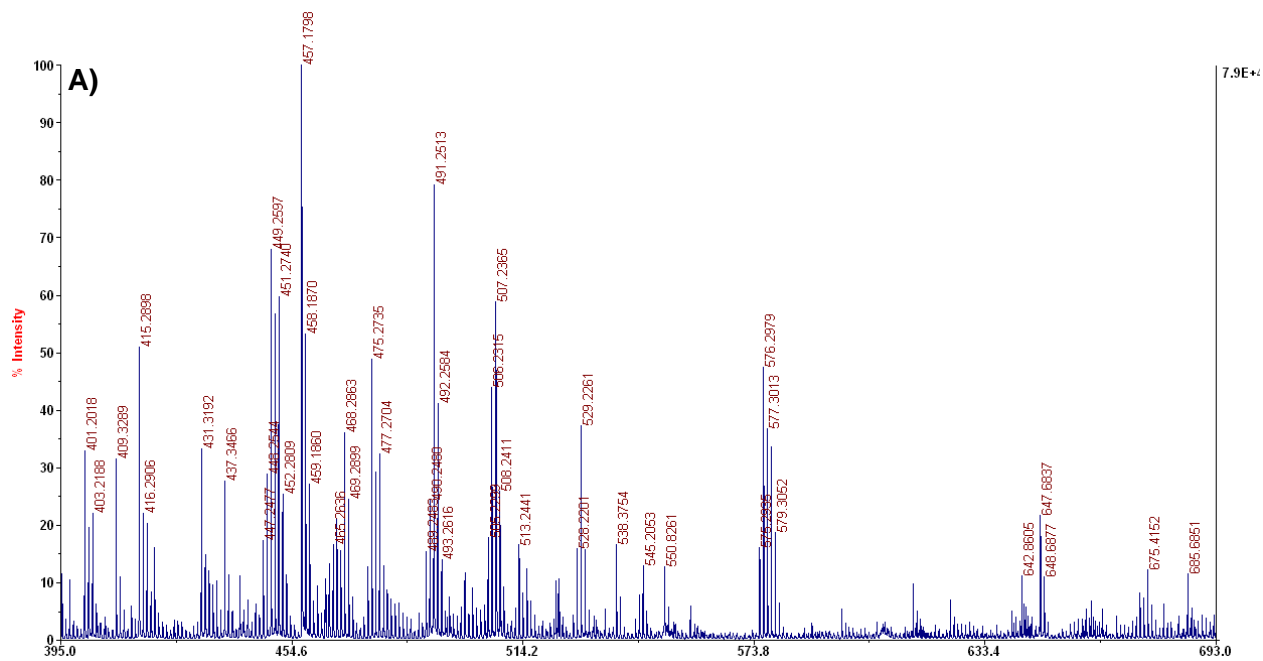
**Figure S16C:** HMBC NMR of ET-ECA copolymer at 318K in  $\text{CDCl}_3$ .

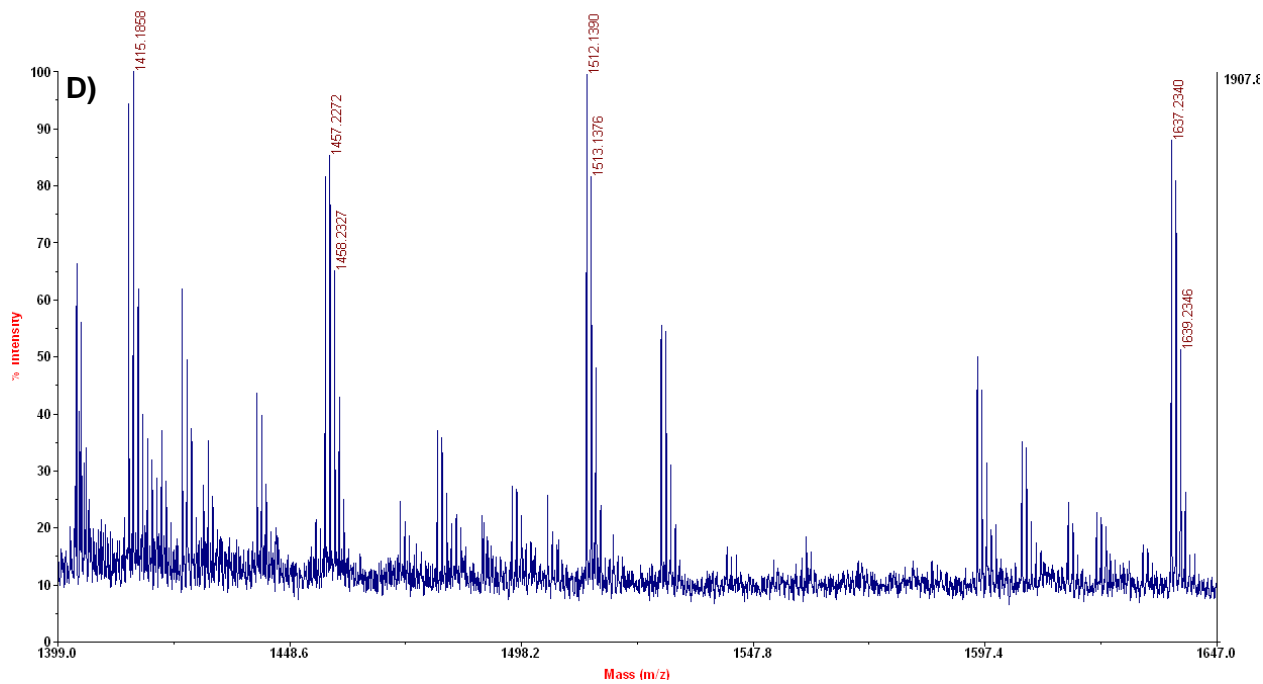
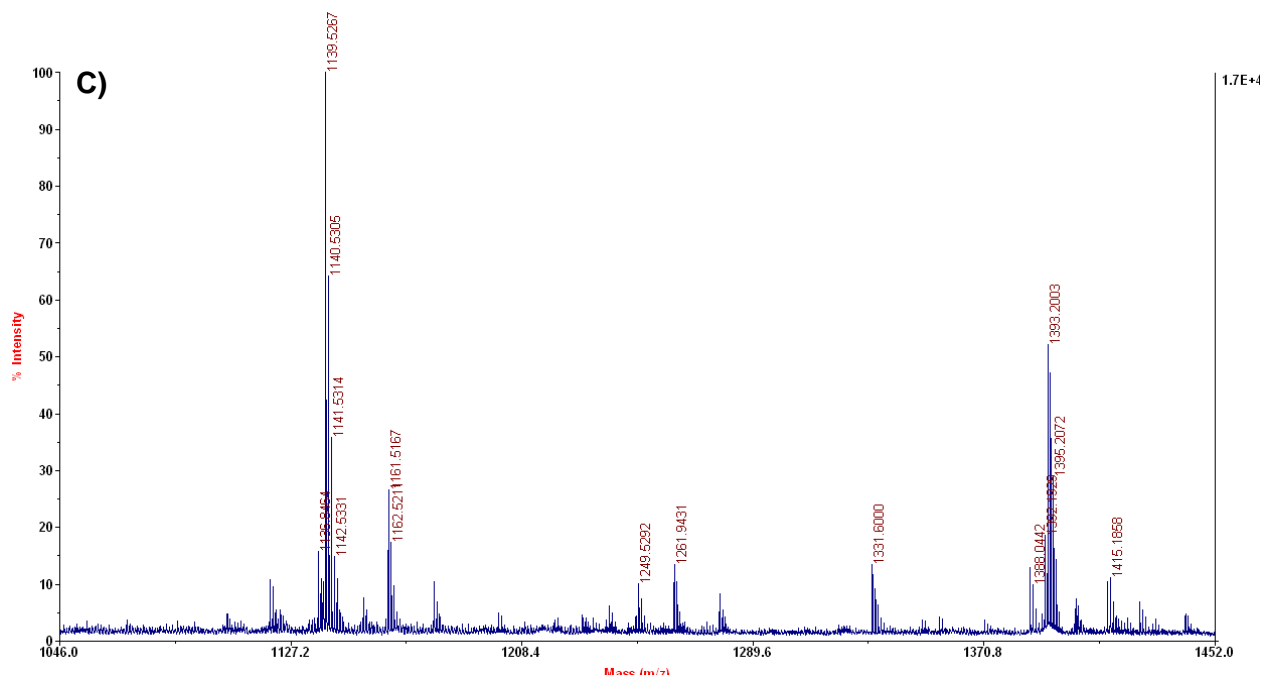


**Figure S16D:** Edited HMBC (expanded) NMR of ET-ECA copolymer at 318K in  $\text{CDCl}_3$ .

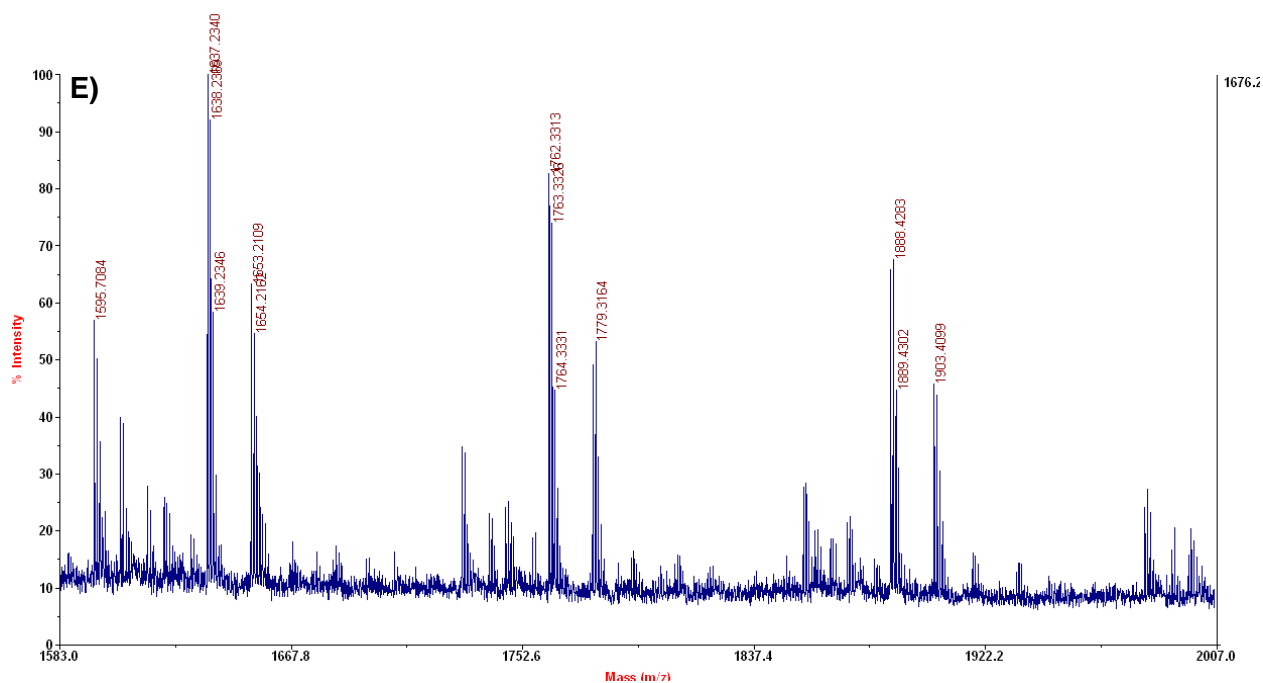


**Figure S16E:** Stacked <sup>1</sup>H COSY NMR spectra of ET-ECA copolymer (black cross peaks) and ECA homopolymer (blue cross peaks) at 318K in CDCl<sub>3</sub>.







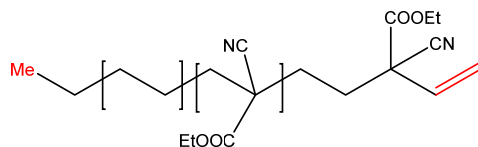


**Figure S17:** MALDI-ToF-MS spectra (A-E) of a copolymer of ethylene and ethyl-2-cyanoacrylate (table S3, run-S3-3).

**Table S4:** MALDI-ToF-MS of copolymers of ethylene–ethyl-2-cyanoacrylate; CET<sub>x</sub>ECA<sub>y</sub> indicates a copolymer chain of “x” ethylene units and “y” ethyl-2-cyanoacrylate units initiated by Pd-Me group. Similarly, HET<sub>x</sub>ECA<sub>y</sub> indicates a copolymer chain initiated by Pd-hydride group. The following peaks were identified from a set of probabilities reported in table S4A and S4B.

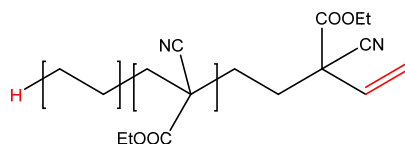
<i>m/z</i>	<i>Copolymer</i>
447.24	CET <sub>11</sub> ECA <sub>1</sub>
895.37	CET <sub>27</sub> ECA <sub>1</sub>
1119.85	CET <sub>35</sub> ECA <sub>1</sub>
1141.49	CET <sub>9</sub> ECA <sub>7</sub>
1393.15	CET <sub>18</sub> ECA <sub>7</sub>
1634.18	CET <sub>40</sub> ECA <sub>4</sub>
1759.18	CET <sub>40</sub> ECA <sub>5</sub>
1884.4	CET <sub>40</sub> ECA <sub>6</sub>

**Table S4A:** Ethylene and ethyl-2-cyanoacrylate permutations and combinations with olefin insertion in a Pd-Me bond.

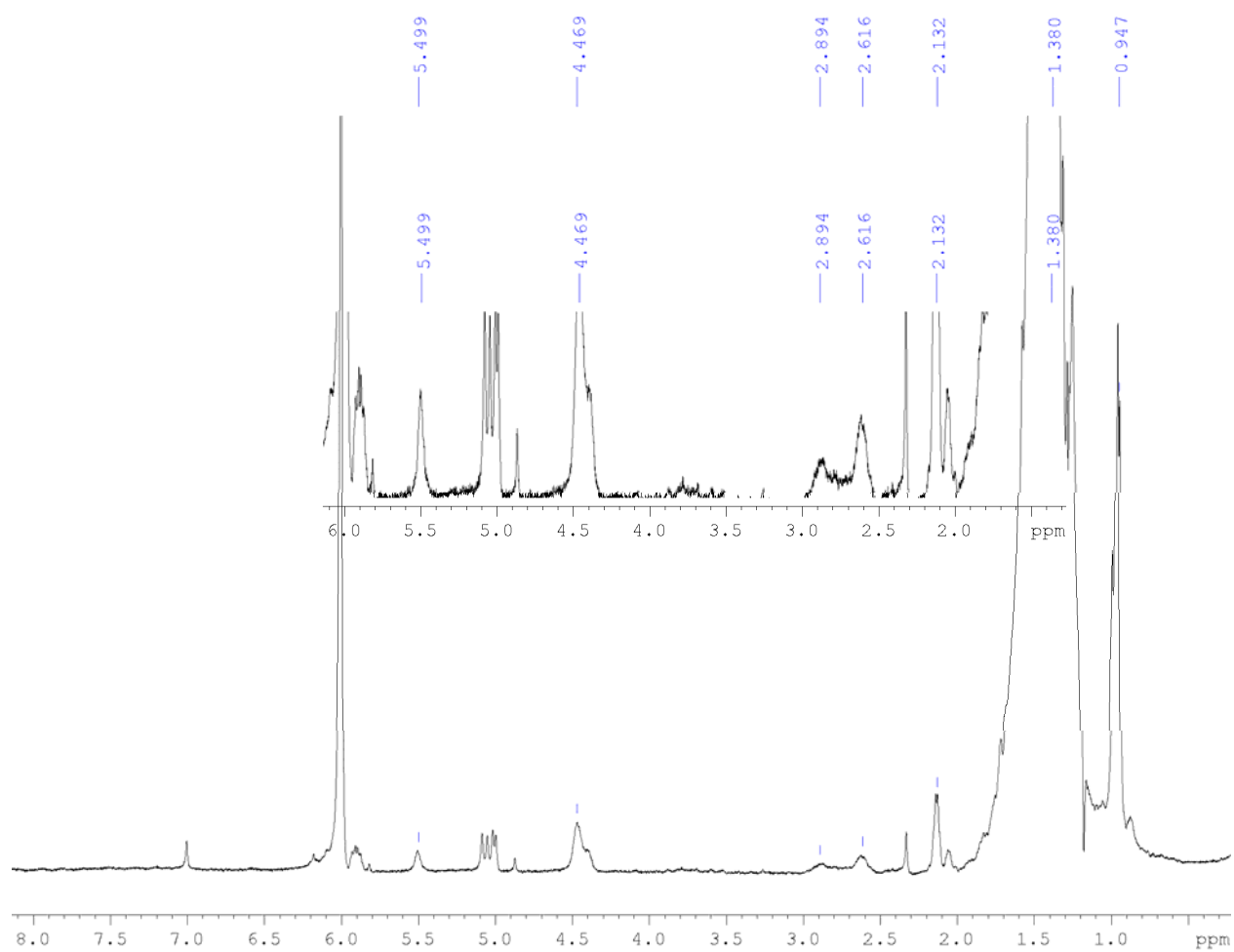


<i>n</i>	<i>CETnCA1</i>	<i>CETnCA2</i>	<i>CETnCA3</i>	<i>CETnCA4</i>	<i>CETnCA5</i>	<i>CETnCA6</i>	<i>CETnCA7</i>
5	279	404	529	654	779	904	1029
6	307	432	557	682	807	932	1057
7	335	460	585	710	835	960	1085
8	363	488	613	738	863	988	1113
9	391	516	641	766	891	1016	1141
10	419	544	669	794	919	1044	1169
11	447	572	697	822	947	1072	1197
12	475	600	725	850	975	1100	1225
13	503	628	753	878	1003	1128	1253
14	531	656	781	906	1031	1156	1281
15	559	684	809	934	1059	1184	1309
16	587	712	837	962	1087	1212	1337
17	615	740	865	990	1115	1240	1365
18	643	768	893	1018	1143	1268	1393
19	671	796	921	1046	1171	1296	1421
20	699	824	949	1074	1199	1324	1450
21	727	852	977	1102	1227	1352	1477
22	755	880	1005	1132	1255	1380	1505
23	783	908	1033	1158	1283	1408	1533
24	811	936	1061	1186	1311	1436	1561
25	839	964	1089	1214	1339	1464	1589
26	867	992	1117	1242	1367	1492	1617
27	895	1020	1145	1270	1395	1520	1645
28	923	1048	1173	1298	1423	1548	1673
29	951	1076	1201	1326	1451	1576	1701
30	979	1104	1229	1354	1479	1604	1729
31	1007	1132	1257	1382	1507	1632	1757
32	1035	1160	1285	1410	1535	1660	1785
33	1063	1188	1313	1438	1563	1688	1813
34	1091	1216	1341	1466	1591	1716	1841
35	1119	1244	1369	1494	1619	1744	1869
36	1147	1272	1397	1522	1647	1772	1897
37	1175	1300	1425	1550	1675	1800	1925
38	1203	1328	1453	1578	1703	1828	1953
39	1231	1356	1481	1606	1731	1856	1981
40	1259	1384	1509	1634	1759	1884	2009

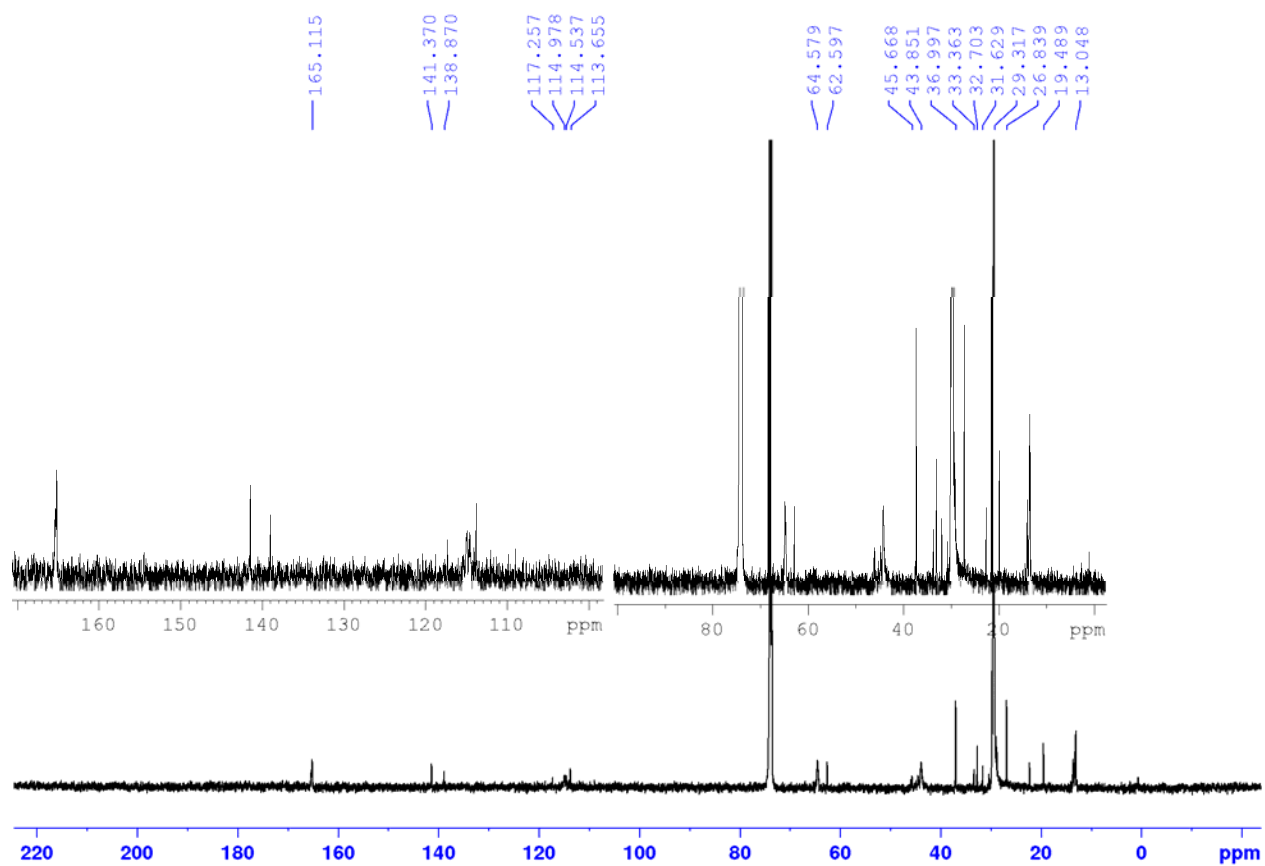
**Table S4B:** Ethylene and ethyl-2-cyanoacrylate permutations and combinations with olefin insertion in a Pd-H bond.



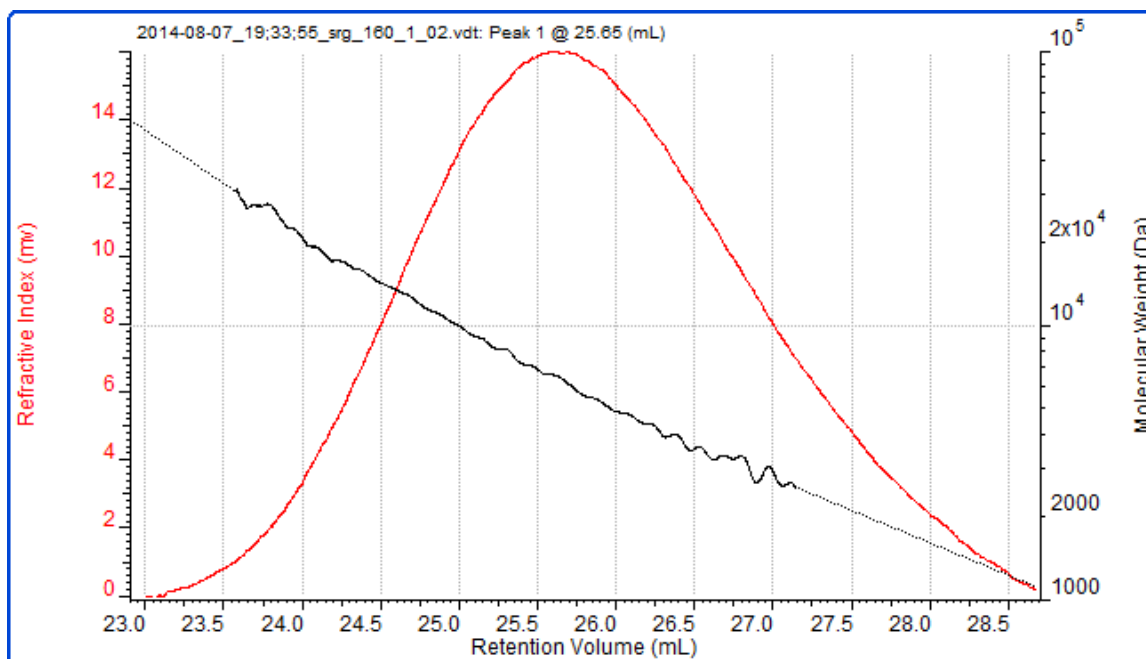
<i>n</i>	HETnCA1	HETnCA2	HETnCA3	HETnCA4	HETnCA5	HETnCA6	HETnCA7
5	265	390	515	640	765	890	1015
6	293	418	543	668	793	918	1043
7	321	446	571	696	821	946	1071
8	349	474	599	724	849	974	1099
9	377	502	627	752	877	1002	1127
10	405	530	655	780	905	1030	1155
11	433	558	683	808	933	1058	1183
12	461	586	711	836	961	1086	1211
13	489	614	739	864	989	1114	1239
14	517	642	767	892	1017	1142	1267
15	545	670	795	920	1045	1170	1295
16	573	698	823	948	1073	1198	1323
17	601	726	851	976	1101	1226	1351
18	629	754	879	1004	1129	1254	1379
19	657	782	907	1032	1157	1282	1407
20	685	810	935	1060	1185	1310	1436
21	713	838	963	1088	1213	1338	1463
22	741	866	991	1118	1241	1366	1491
23	769	894	1019	1144	1269	1394	1519
24	797	922	1047	1172	1297	1422	1547
25	825	950	1075	1200	1325	1450	1575
26	853	978	1103	1228	1353	1478	1603
27	881	1006	1131	1256	1381	1506	1631
28	909	1034	1159	1284	1409	1534	1659
29	937	1062	1187	1312	1437	1562	1687
30	965	1090	1215	1340	1465	1590	1715
31	993	1118	1243	1368	1493	1618	1743
32	1021	1146	1271	1396	1521	1646	1771
33	1049	1174	1299	1424	1549	1674	1799
34	1077	1202	1327	1452	1577	1702	1827
35	1105	1230	1355	1480	1605	1730	1855
36	1133	1258	1383	1508	1633	1758	1883
37	1161	1286	1411	1536	1661	1786	1911
38	1189	1314	1439	1564	1689	1814	1939
39	1217	1342	1467	1592	1717	1842	1967
40	1245	1370	1495	1620	1745	1870	1995



**Figure S18:**  $^1\text{H}$  NMR of ET-ECA copolymer in  $\text{C}_2\text{D}_2\text{Cl}_4$  at 403K (TableS3, S3-1).



**Figure S19:**  $^{13}\text{C}$  NMR of ET-ECA copolymer in  $\text{C}_2\text{D}_2\text{Cl}_4$  at 403K (Table S3, S3-1).



Data File: 2014-08-07\_19:33:55\_srg\_160\_1\_02.vdt Method: Aug2014-0004.vcm

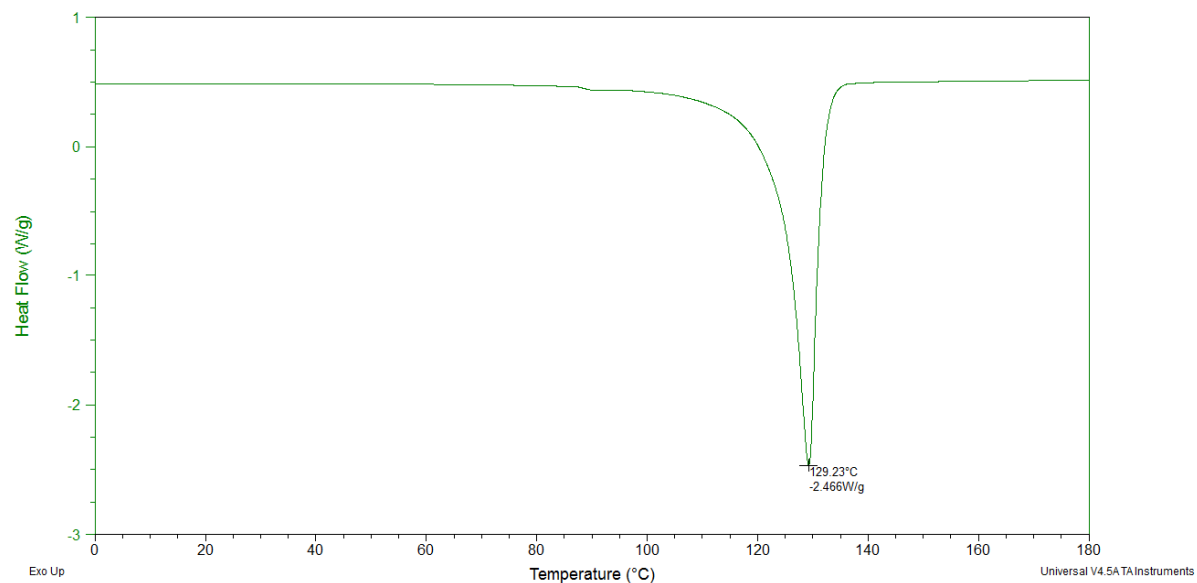
Mn - (Daltons)	4,706
Mw - (Daltons)	7,240
Mz - (Daltons)	11,190
Mp - (Daltons)	6,340
Mw / Mn	1.538

**Figure S20:** High temperature (HT)-GPC chromatogram of ET-ECA copolymer in trichlorobenzene at 160°C (Table S3, S3-1).

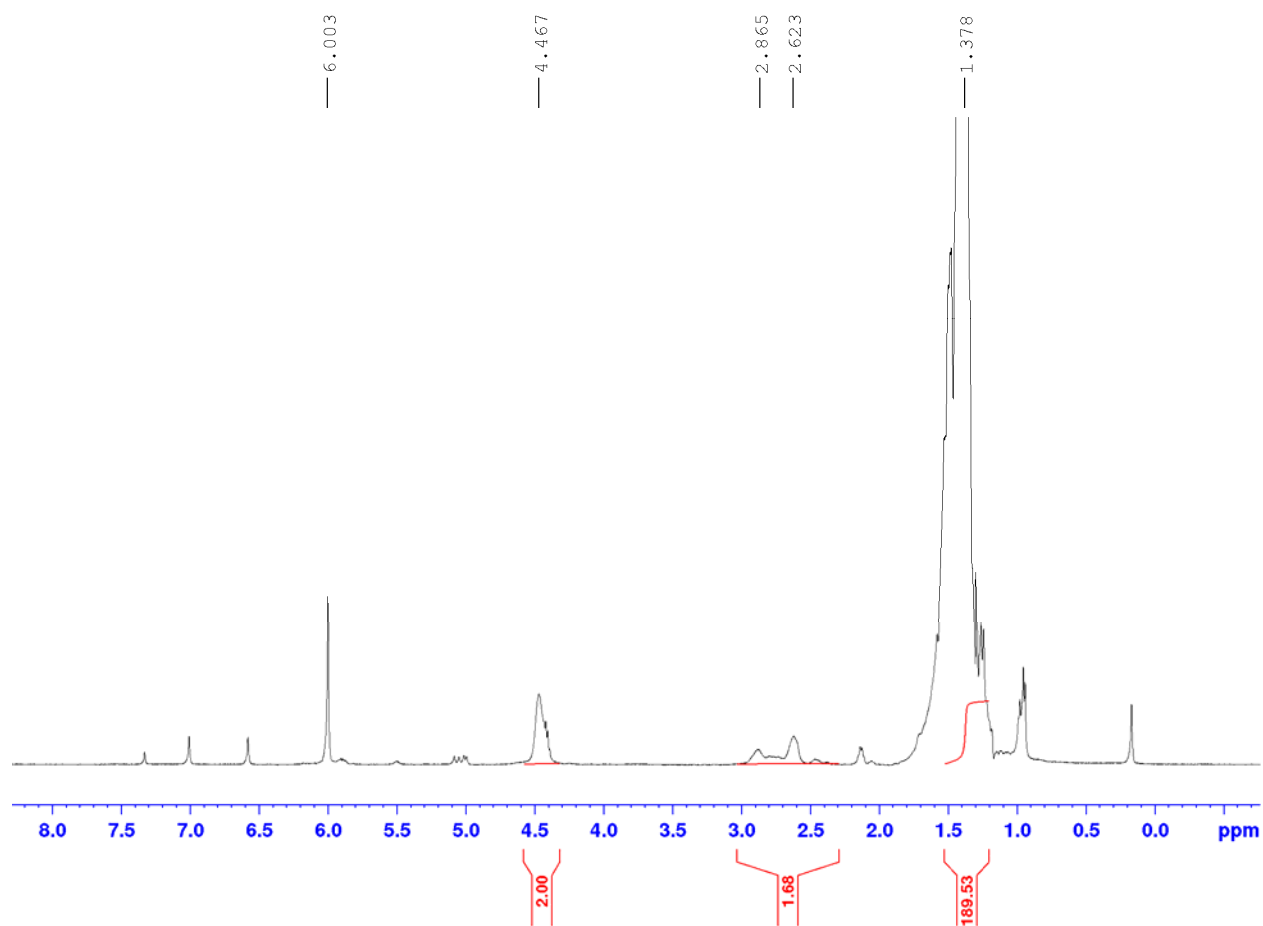
Sample: srg-160  
Size: 3.8000 mg  
Method: Megha

DSC

File: E:\...aug 2014\srg\_160\srg-160  
Operator: shahaji  
Run Date: 11-Aug-2014 15:44  
Instrument: DSC Q10 V9.0 Build 275

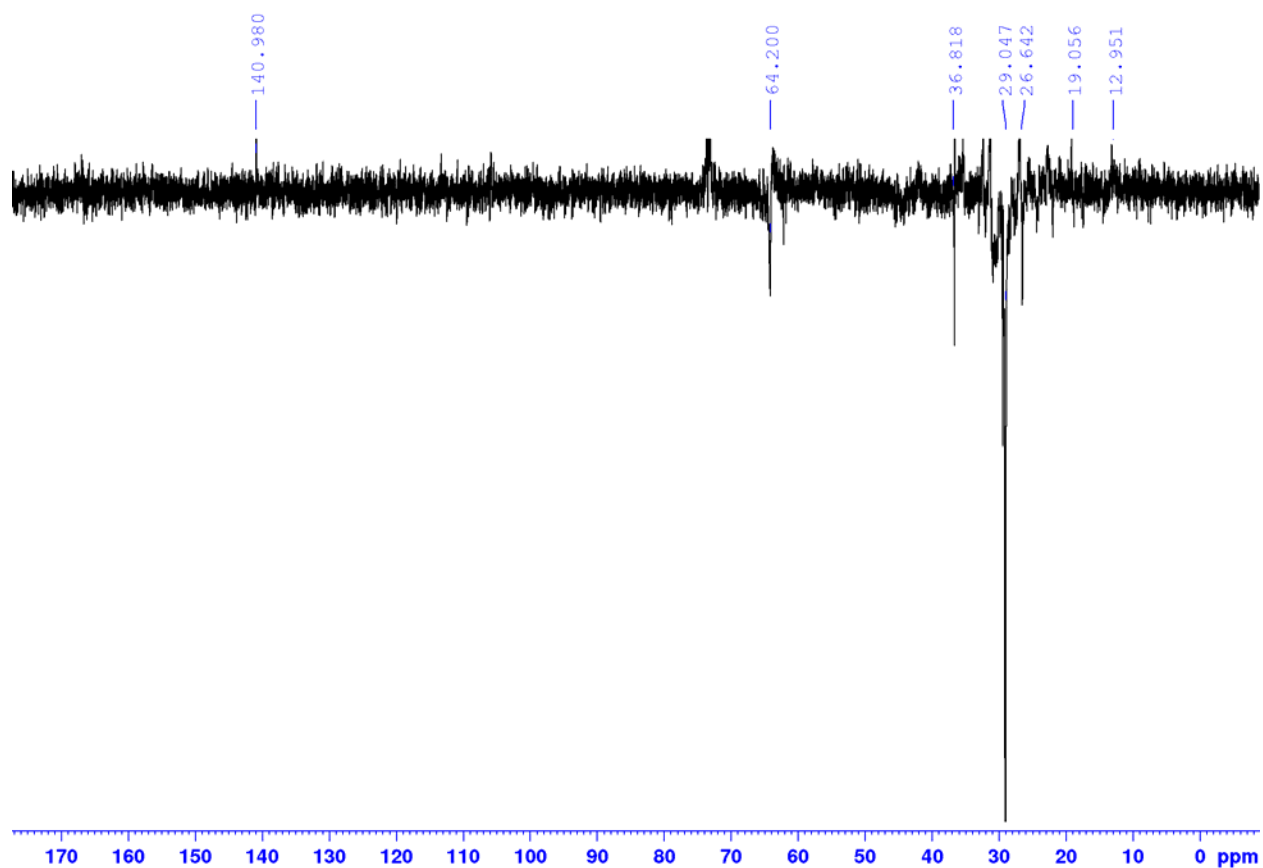


**Figure S21:** DSC heating (2<sup>nd</sup>) curve of ET-ECA copolymer (Table S3, S3-1).

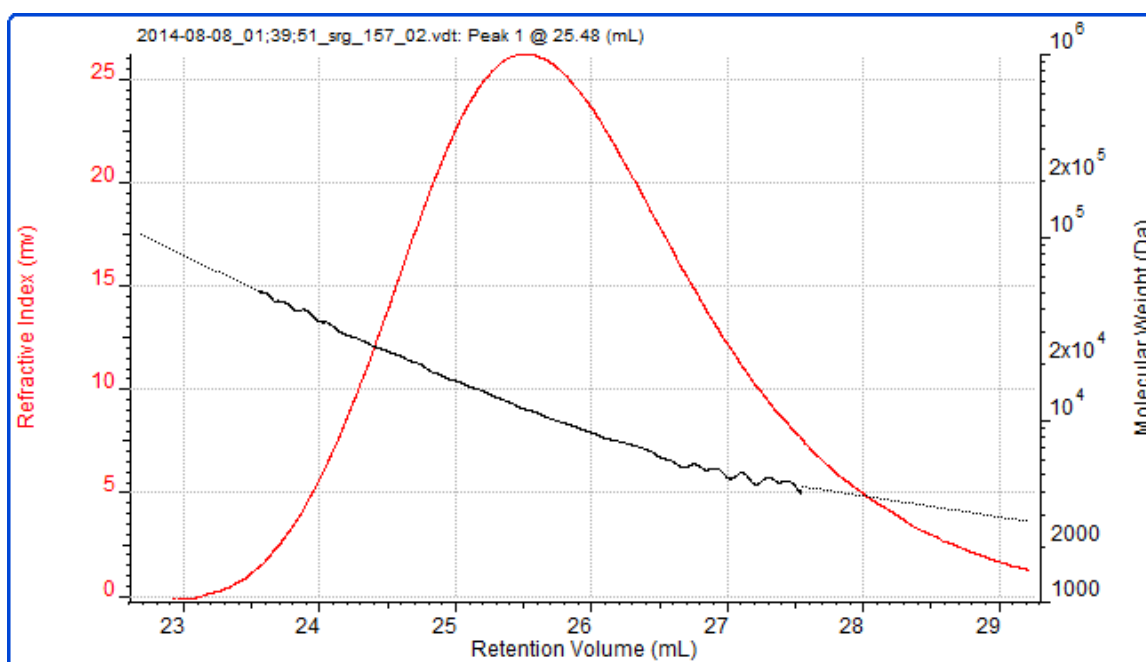


**Figure S22:**  $^1\text{H}$  NMR of ET-ECA copolymer in  $\text{C}_2\text{D}_2\text{Cl}_4$  at 403K (TableS3, S3-2).



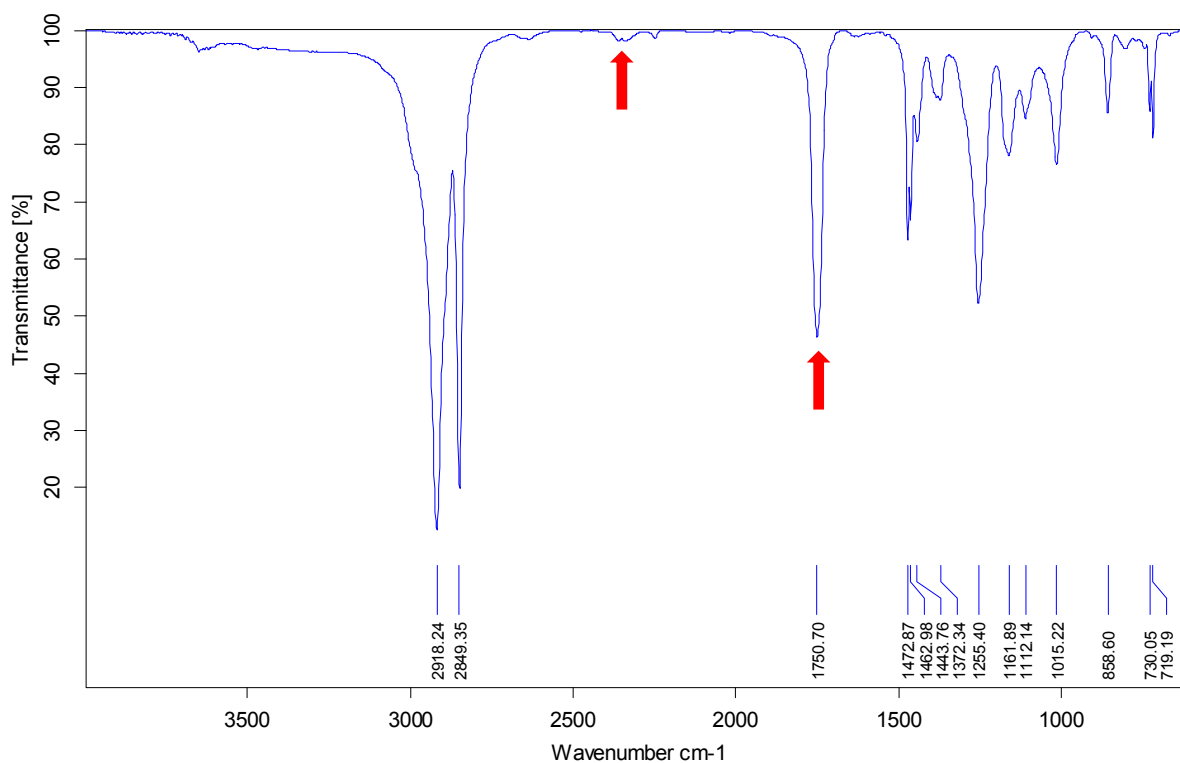


**Figure S23:** DEPT-135 NMR of ET-ECA copolymer in  $C_2D_2Cl_4$  at 403K (Table S3, S3-2).



Data File: 2014-08-08_01;39;51_srg_157_02.vdt Method: Aug2014-0003.vcm	
Mn - (Daltons)	8,194
Mw - (Daltons)	11,993
Mz - (Daltons)	17,818
Mp - (Daltons)	11,361
Mw / Mn	1.464

**Figure S24:** High temperature (HT)-GPC chromatogram of ET-ECA copolymer in trichlorobenzene at 160°C (Table S3, S3-2).



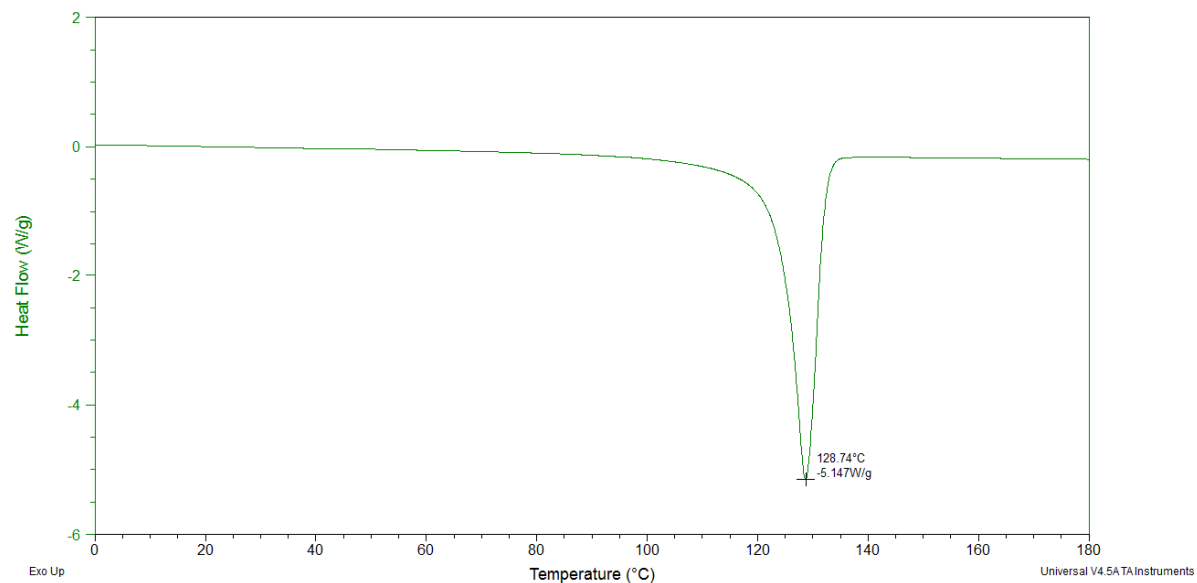
D:\De Samir Chikali\Shahaji\240714\SRG157.0	Sample description	Sample Compartment	24/07/2014
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**Figure S25:** Infrared spectrum of ET-ECA copolymer (Table S3, S3-2).

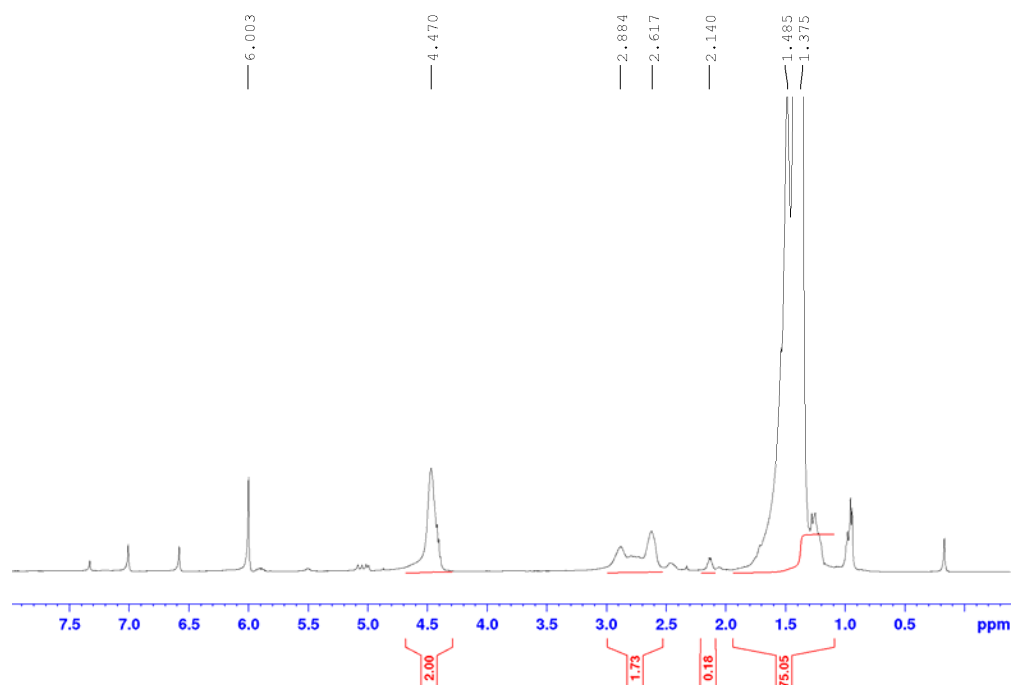
Sample: srg\_157 new  
Size: 4.2000 mg  
Method: Megha

DSC

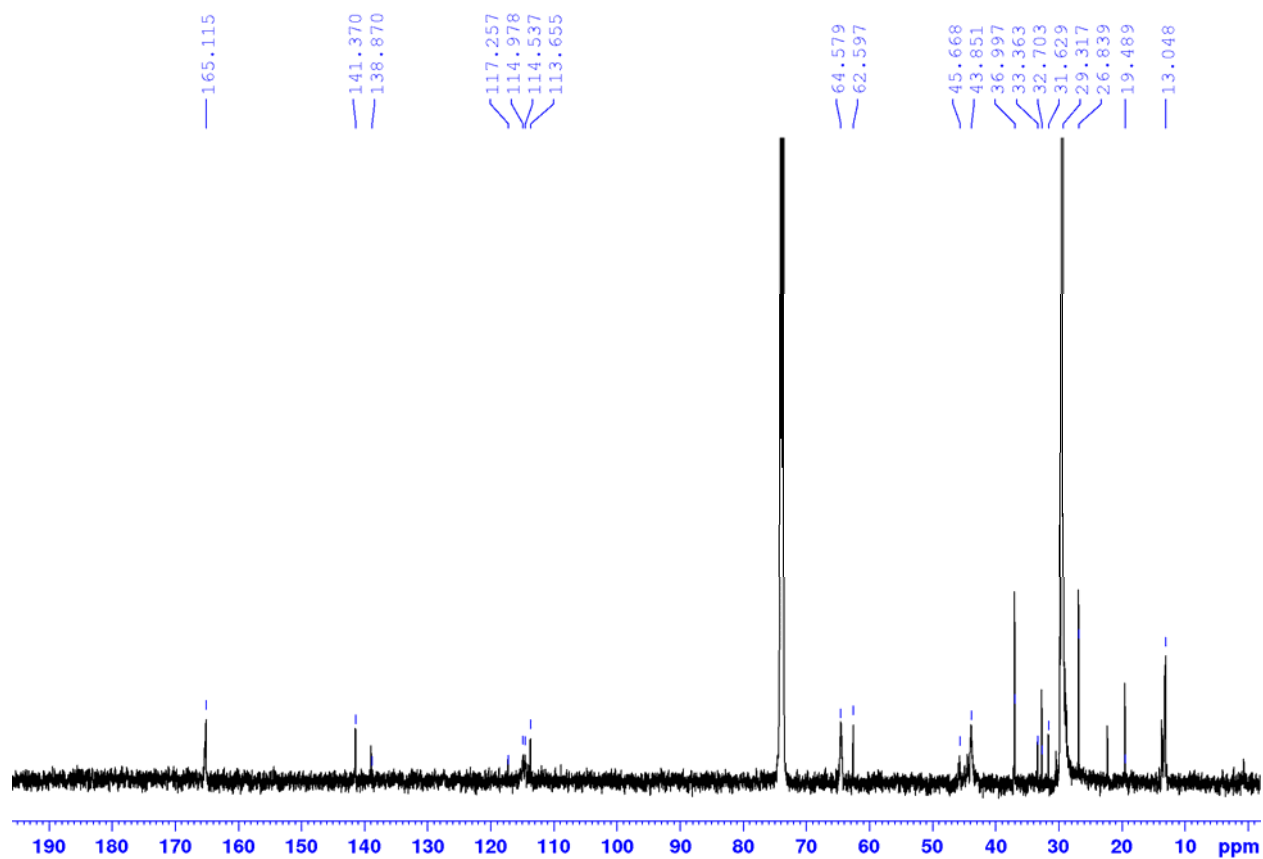
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Operator: shahaji  
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Instrument: DSC Q10 V9.0 Build 275



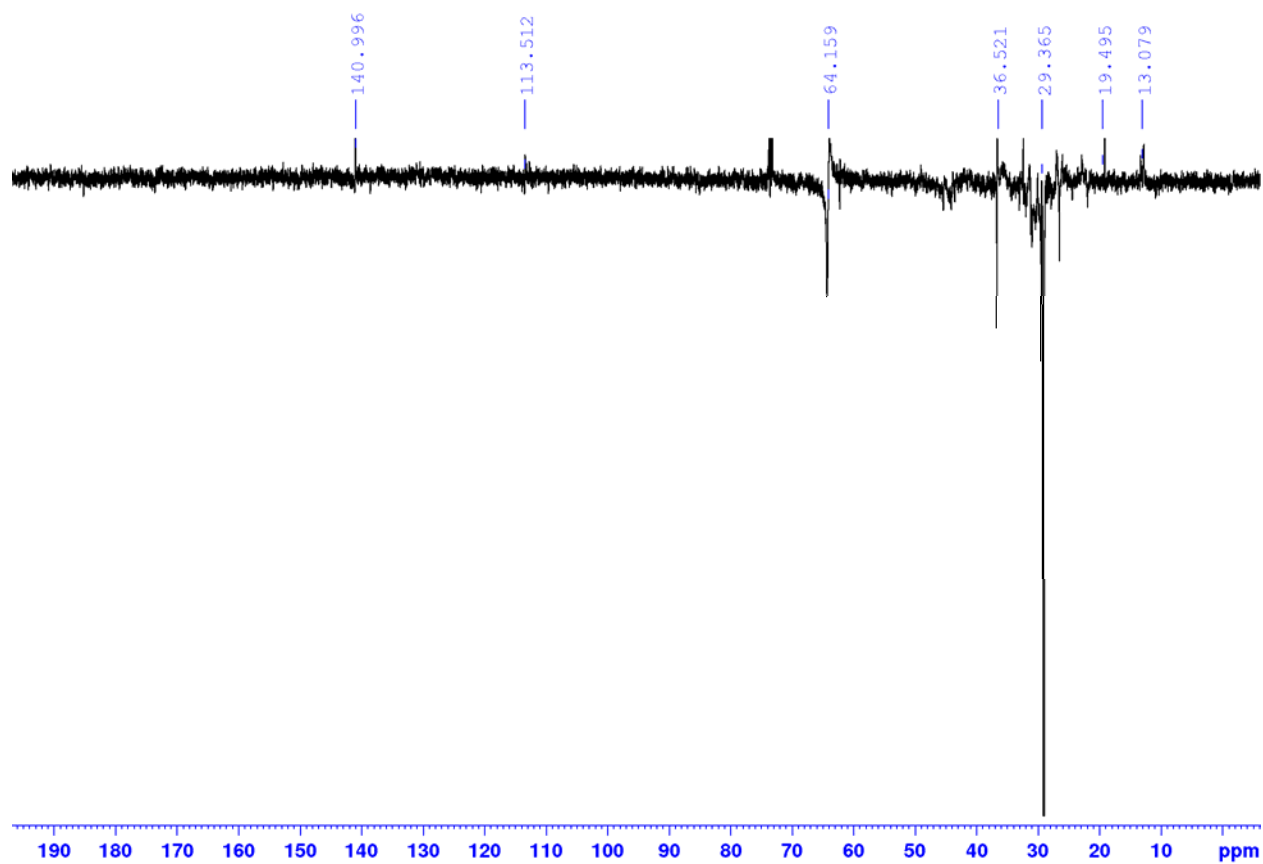
**Figure S26:** DSC heating (2<sup>nd</sup>) curve of ET-ECA copolymer (Table S3, S3-2).



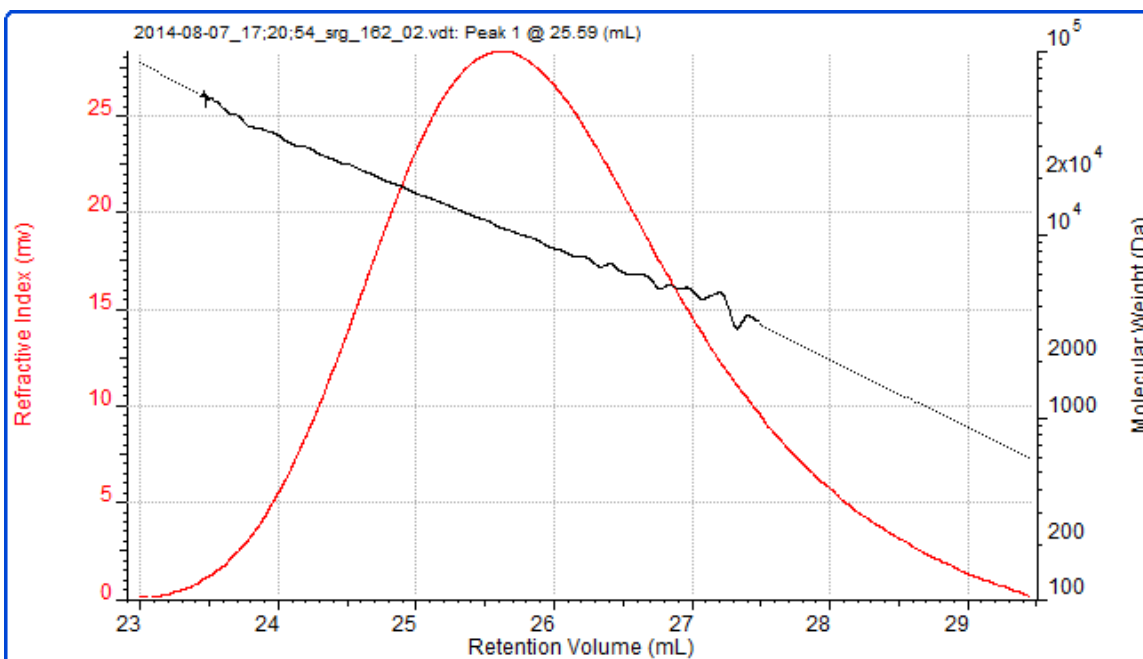
**Figure S27:** <sup>1</sup>H NMR of ET-ECA copolymer in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 403K (TableS3, S3-3).



**Figure S28:**  $^{13}\text{C}$  NMR of ET-ECA copolymer in  $\text{C}_2\text{D}_2\text{Cl}_4$  at 403K (Table S3, S3-3).



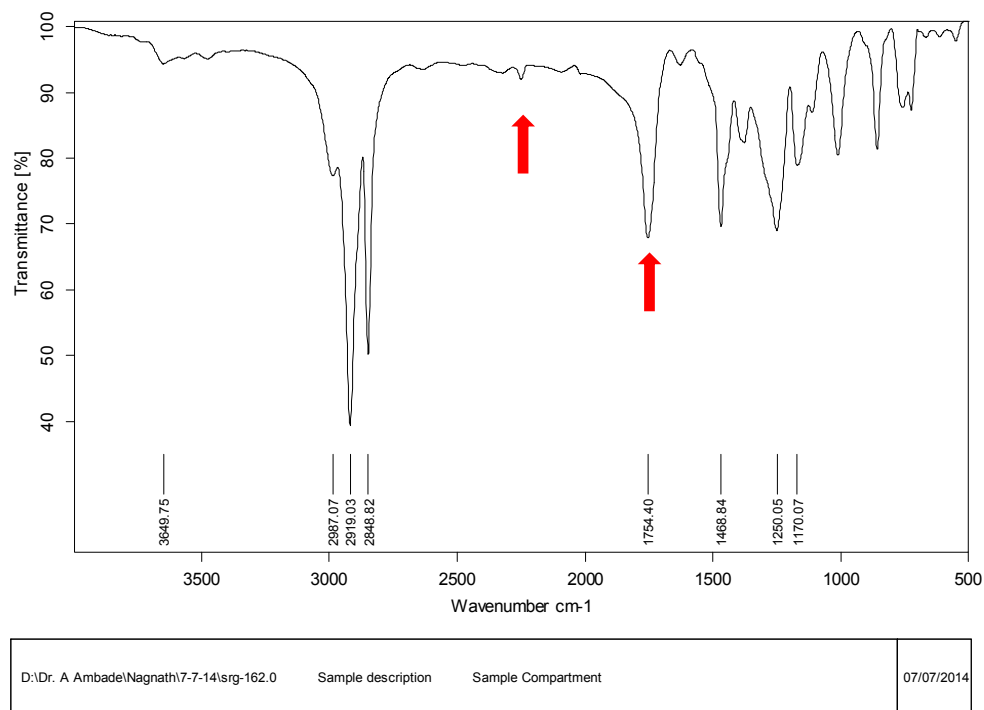
**Figure S29:** DEPT-135 NMR of ET-ECA copolymer in  $C_2D_2Cl_4$  at 403K (Table S3, S3-3).



Data File: 2014-08-07\_17:20:54\_srg\_162\_02.vdt Method: Aug2014-0008.vcm

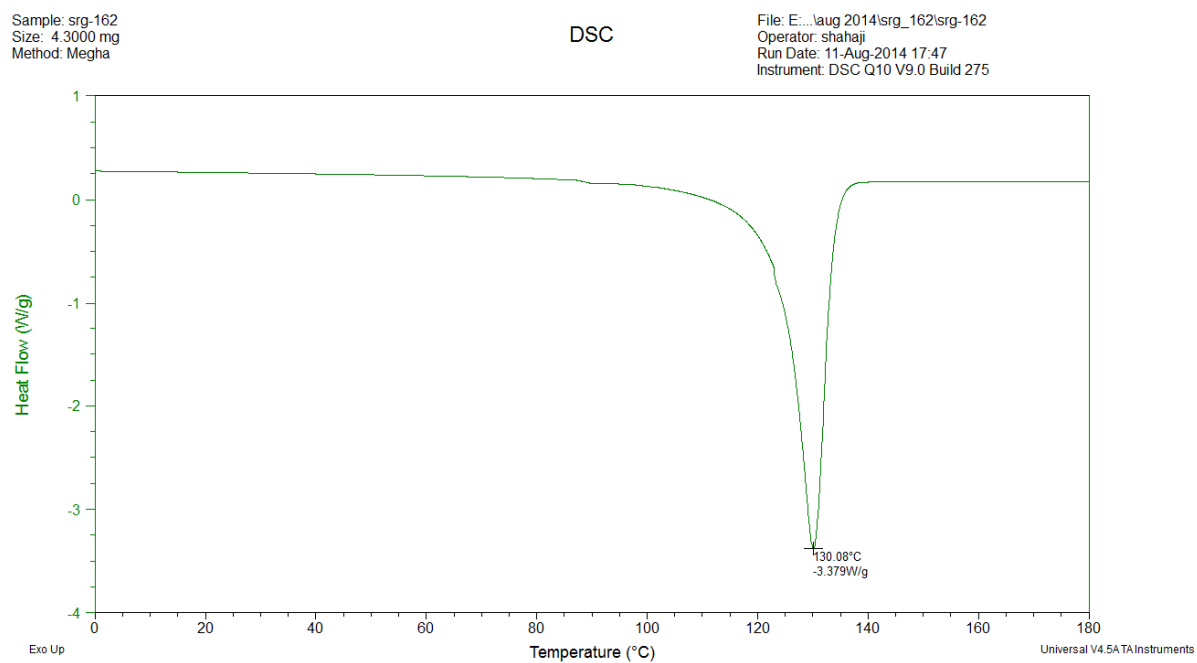
Mn - (Daltons)	6,412
Mw - (Daltons)	11,538
Mz - (Daltons)	17,799
Mp - (Daltons)	10,841
Mw / Mn	1.799

**Figure S30:** High temperature (HT)-GPC chromatogram of ET-ECA copolymer in trichlorobenzene at 160°C (Table S3, S3-3).

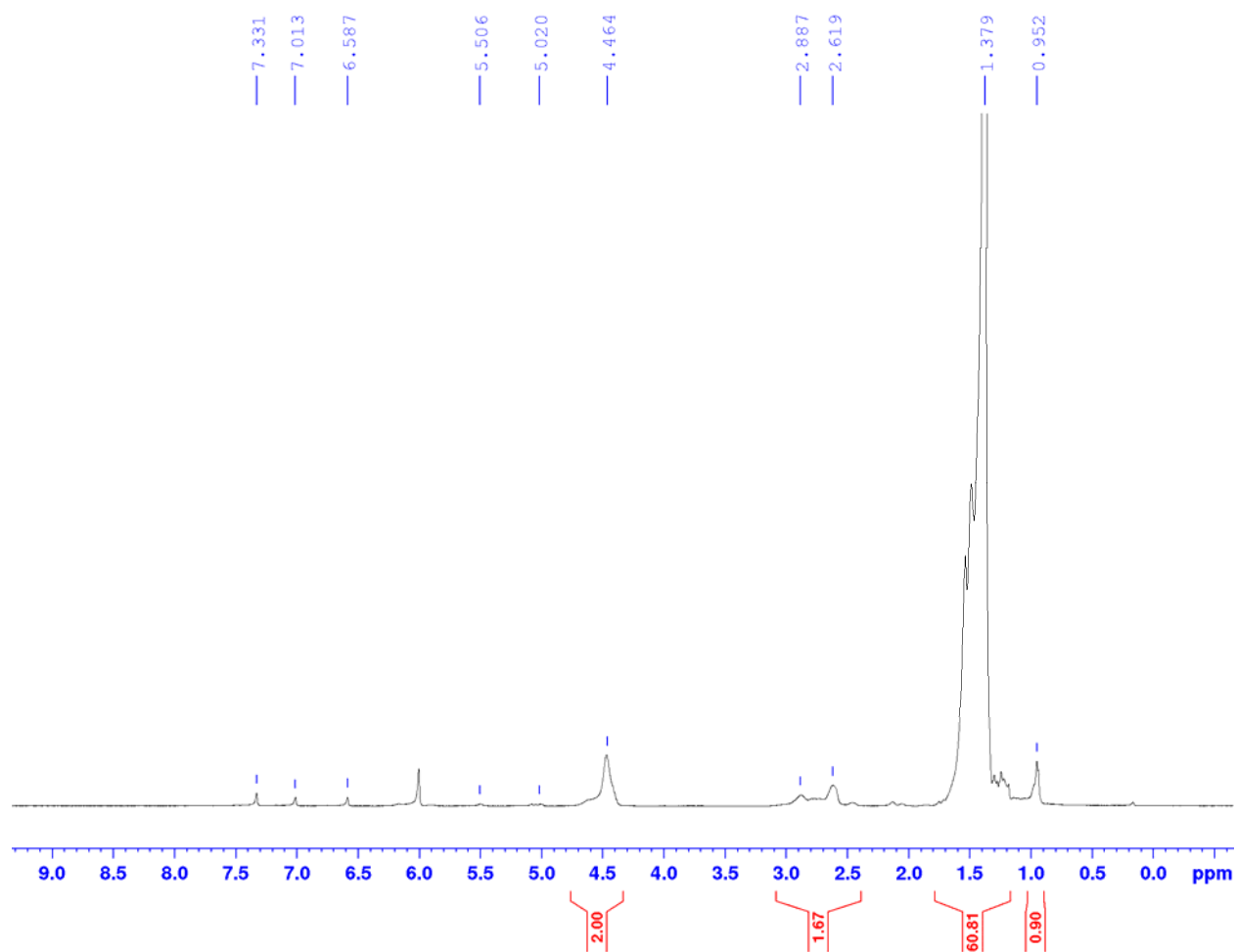


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**Figure S31:** Infrared spectrum of ET-ECA copolymer (Table S3, S3-3).

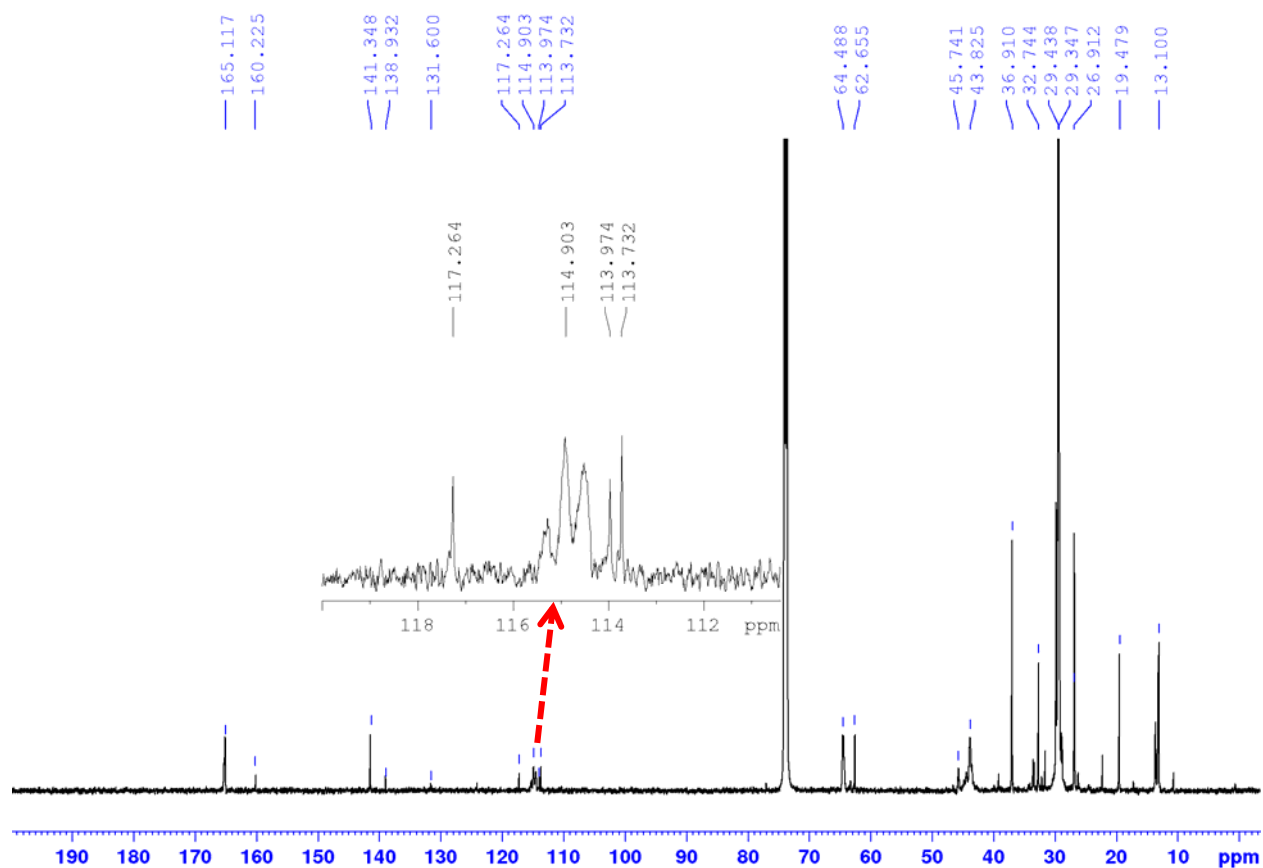


**Figure S32:** DSC heating (2<sup>nd</sup>) curve of ET-ECA copolymer (Table S3, S3-3).

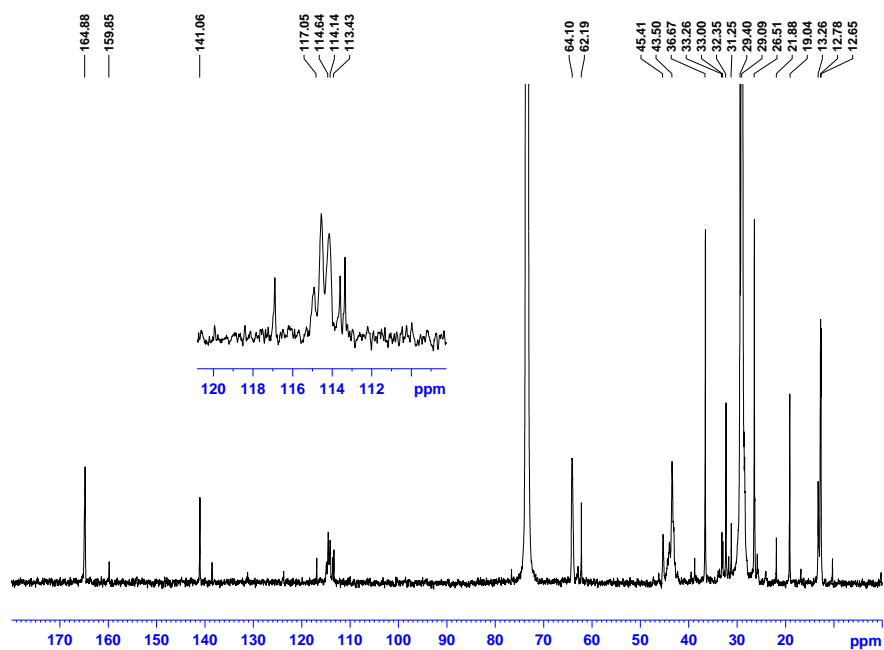


**Figure S33:**  $^1\text{H}$  NMR of ET-ECA copolymer in  $\text{C}_2\text{D}_2\text{Cl}_4$  at 403K (Table S3, S3-4).

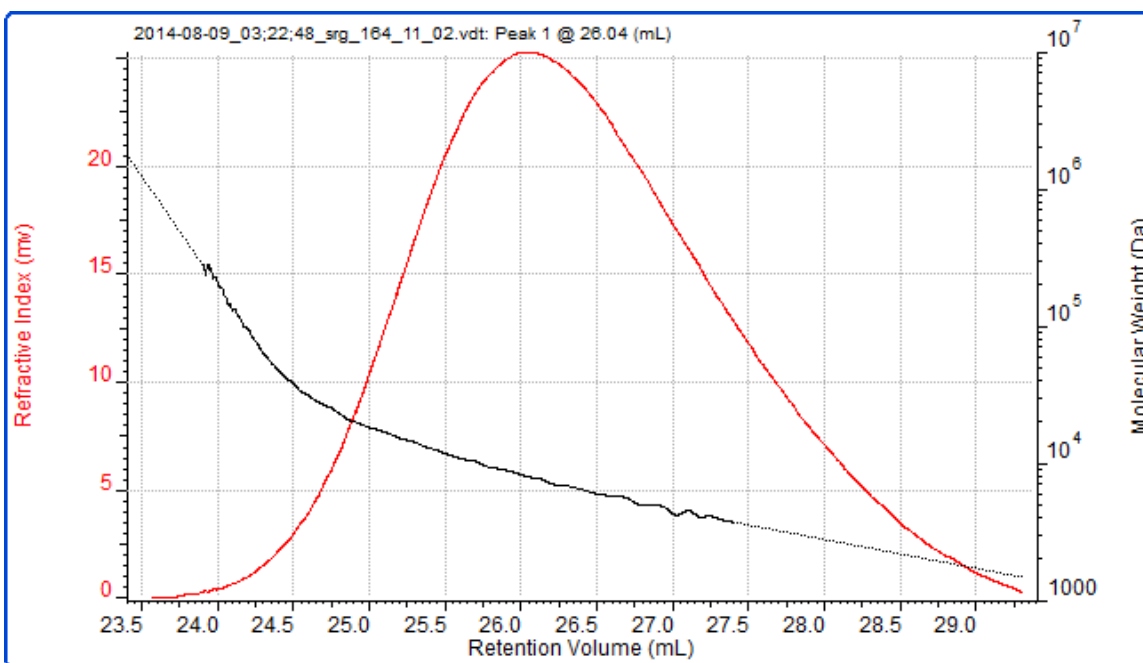




**Figure S34A:**  $^{13}\text{C}$  NMR of ET-ECA copolymer in  $\text{C}_2\text{D}_2\text{Cl}_4$  at 403K (Table S3, S3-4).



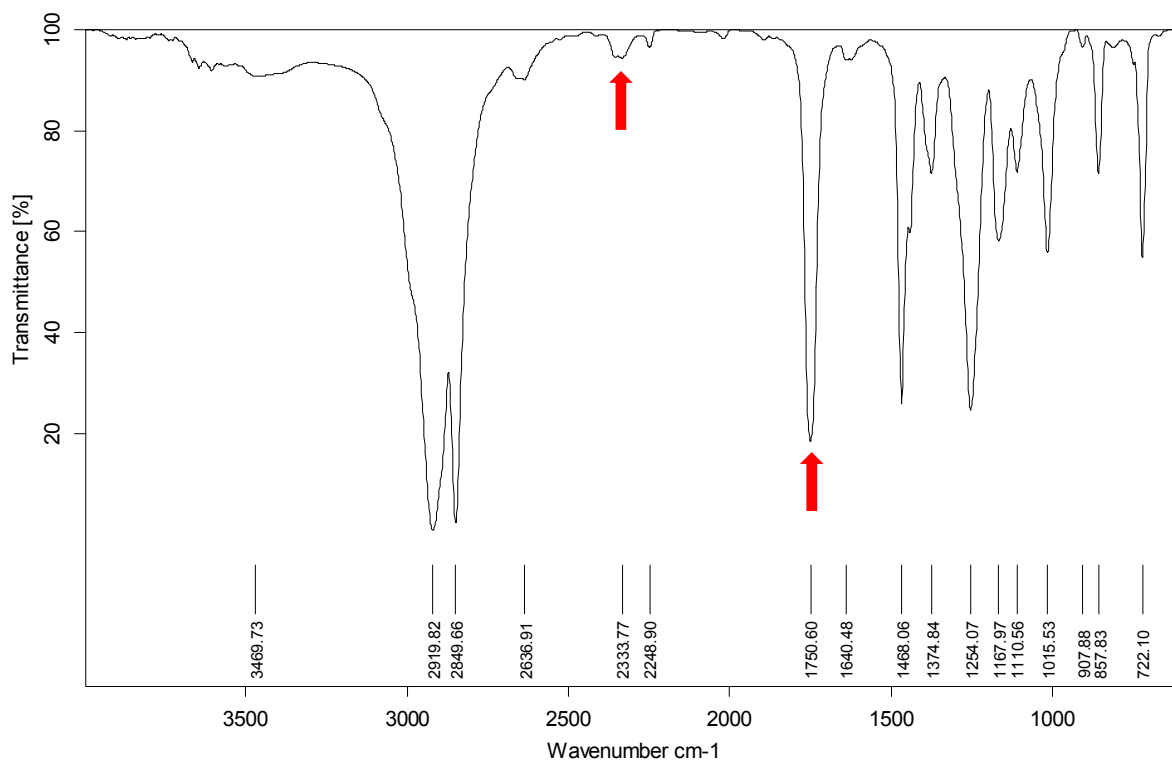
**Figure S34B:** Expanded view of  $^{13}\text{C}$  NMR of ET-ECA copolymer in  $\text{C}_2\text{D}_2\text{Cl}_4$  at 403K (Table S3, S3-4).



Data File: 2014-08-09\_03;22;48\_srg\_164\_11\_02.vdt Method: Aug2014-0003.vcm

Mn - (Daltons)	5,813
Mw - (Daltons)	9,564
Mz - (Daltons)	70,196
Mp - (Daltons)	7,925
Mw / Mn	1.645

**Figure S35:** High temperature (HT)-GPC chromatogram of ET-ECA copolymer in trichlorobenzene at 160°C (Table S3, S3-4).



D:\De Samir Chikali\SRG164.0

Sample description

Sample Compartment

12/07/2014

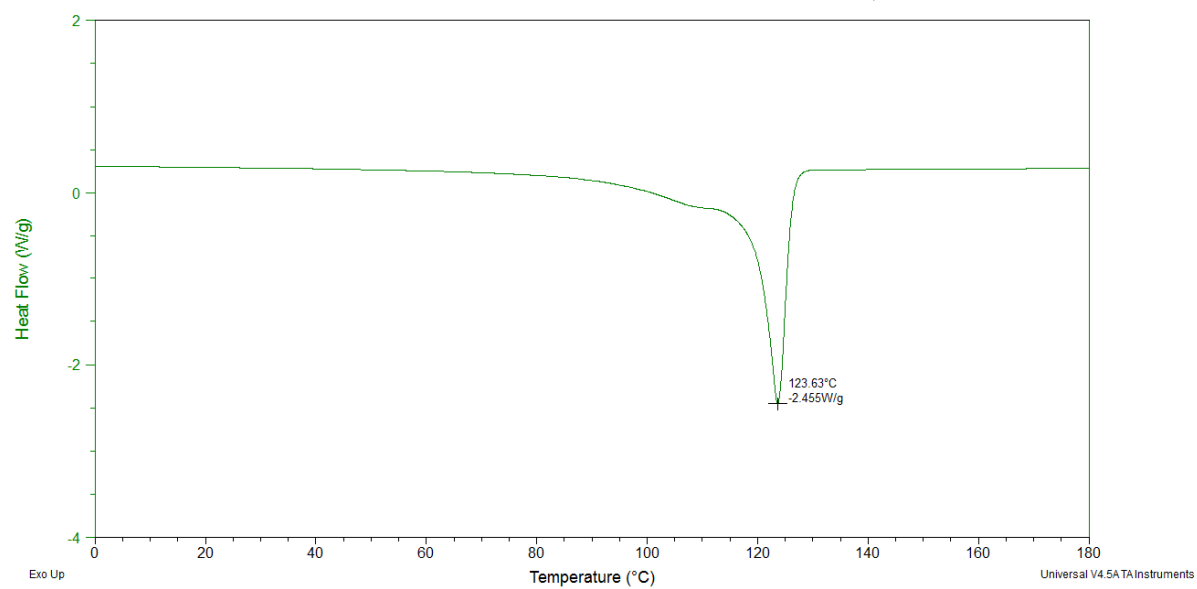
Page 1/1

**Figure S36:** Infrared spectrum of ET-ECA copolymer (Table S3, S3-4).

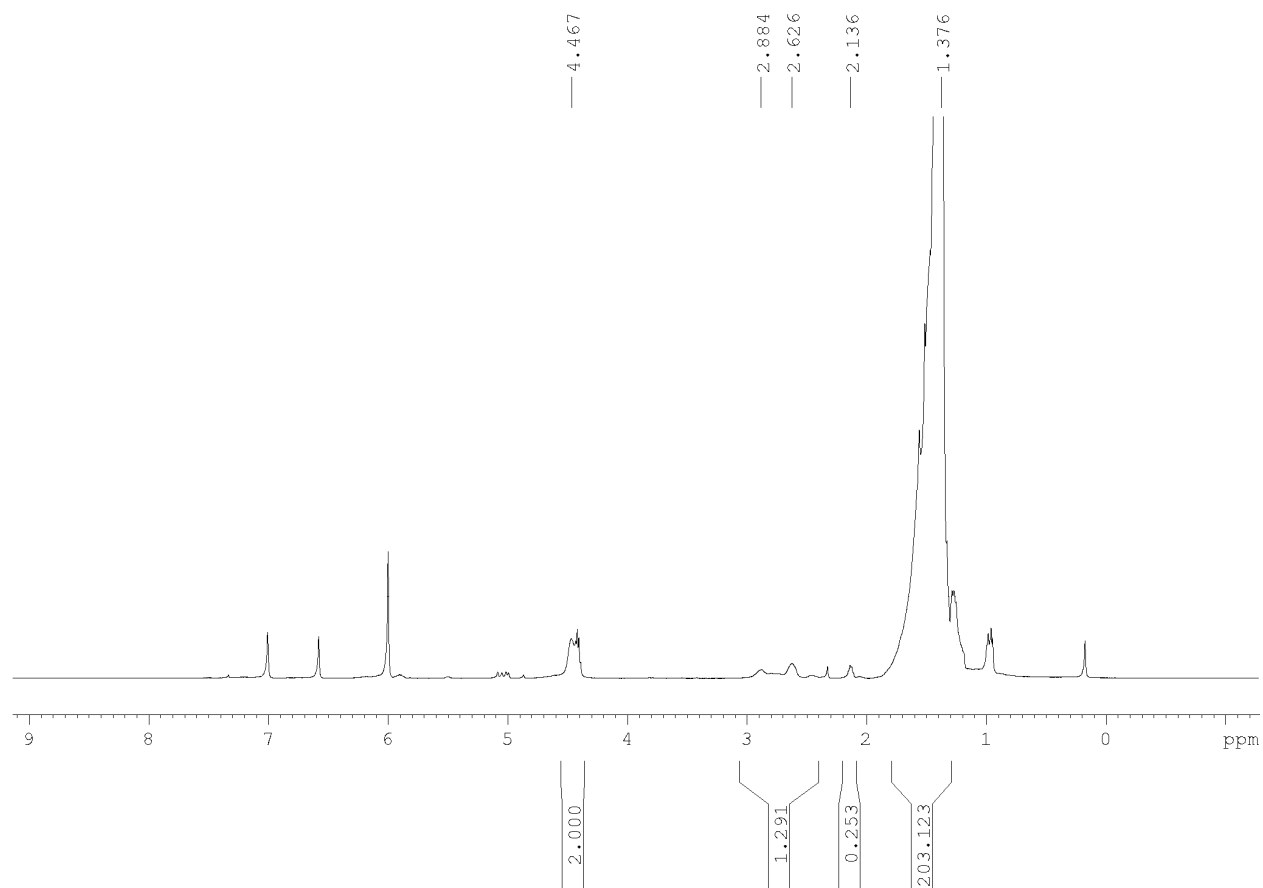
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Size: 3.7000 mg  
Method: Megha

DSC

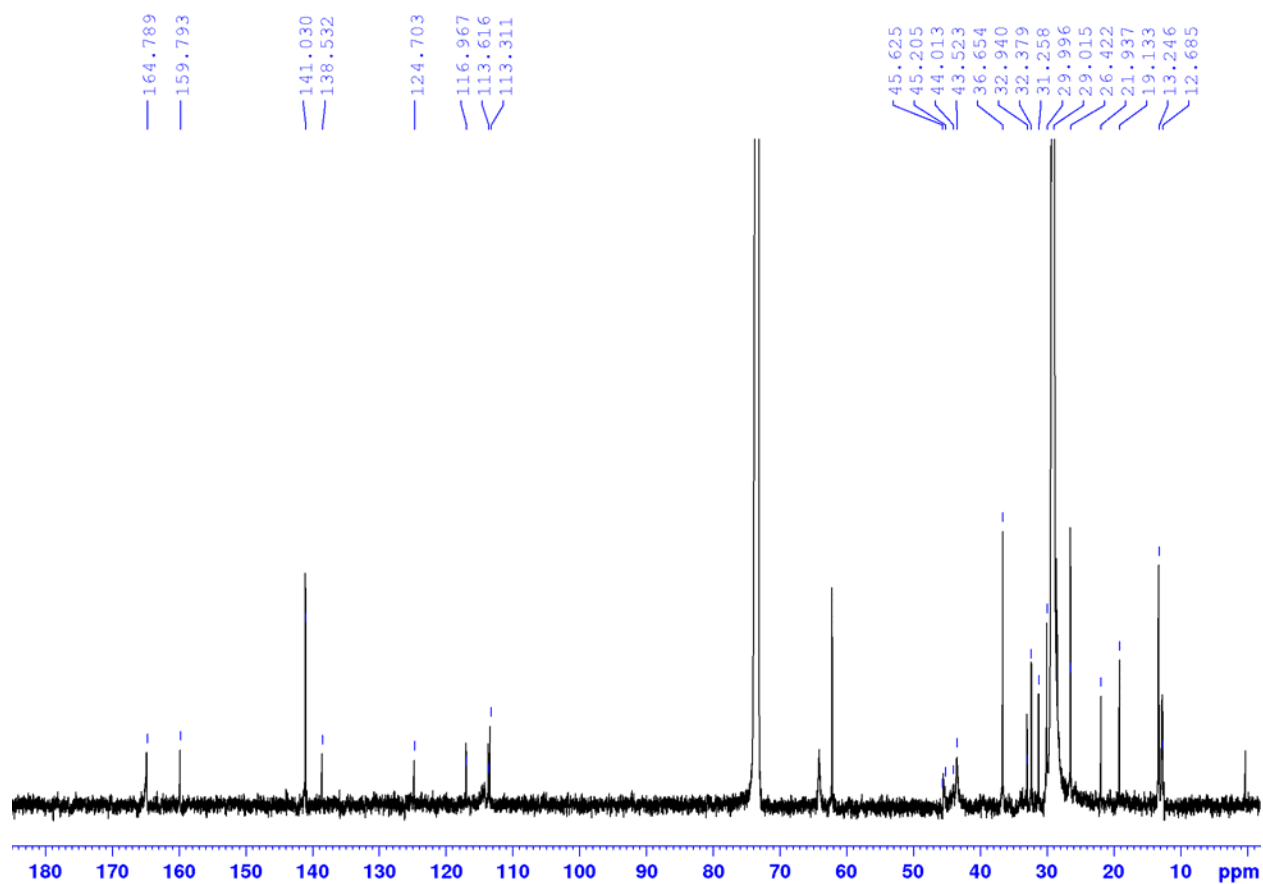
File: E:\New folder\srg\_164R2  
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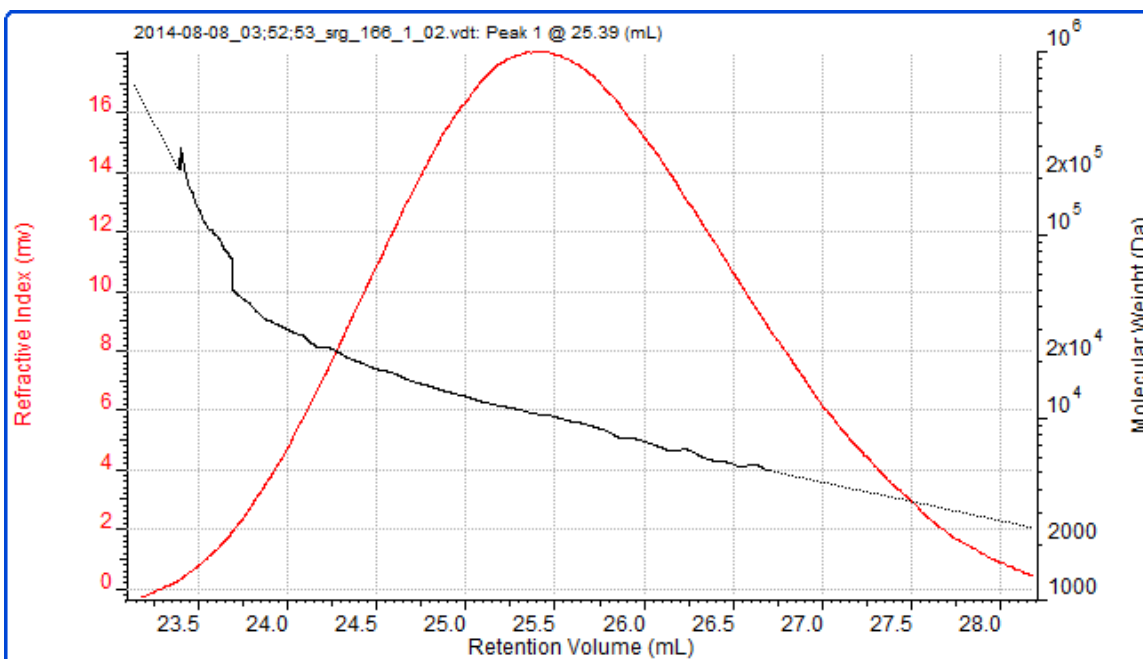
**Figure S37:** DSC thermogram (2<sup>nd</sup> heating cycle) of ET-ECA copolymer (Table S3, S3-4).



**Figure S38:**  $^1\text{H}$  NMR of ET-ECA copolymer in  $\text{C}_2\text{D}_2\text{Cl}_4$  at 403K (Table S3, S3-5).

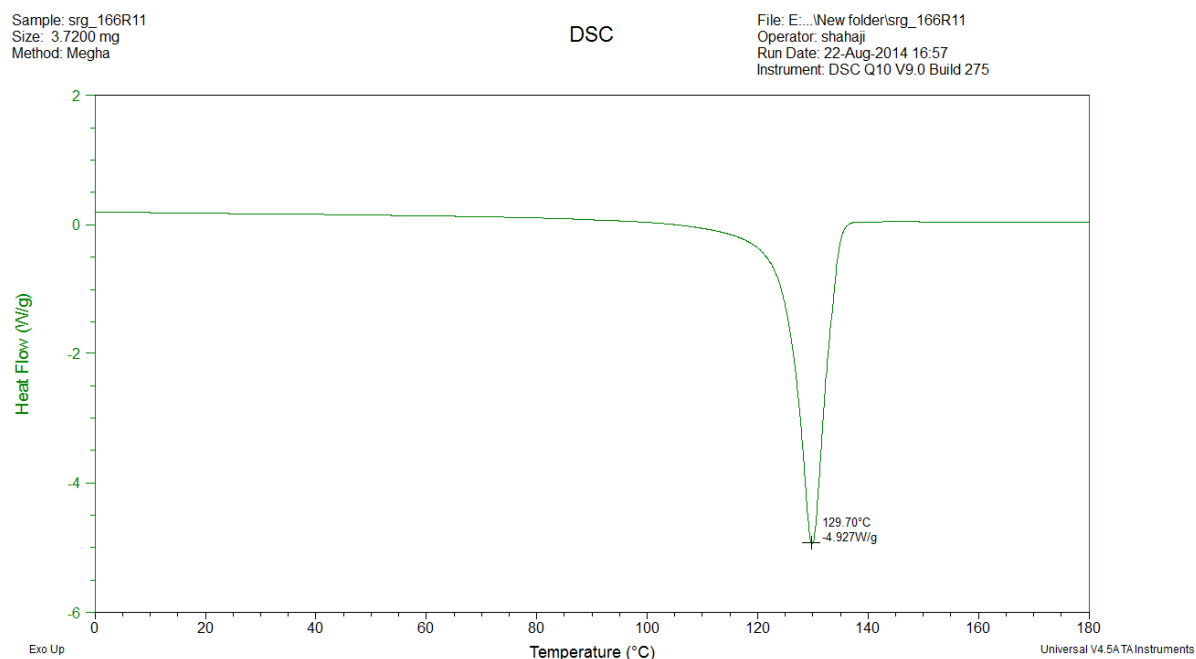


**Figure S39:**  $^{13}\text{C}$  NMR of ET-ECA copolymer in  $\text{C}_2\text{D}_2\text{Cl}_4$  at 403K (Table S3, S3-5).



Data File: 2014-08-08_03;52;53_srg_166_1_02.vdt Method: Aug2014-0003.vcm	
Mn - (Daltons)	8,296
Mw - (Daltons)	12,075
Mz - (Daltons)	33,836
Mp - (Daltons)	10,299
Mw / Mn	1.455

**Figure S40:** High temperature (HT)-GPC chromatogram of ET-ECA copolymer in trichlorobenzene at 160°C (Table S3, S3-5).

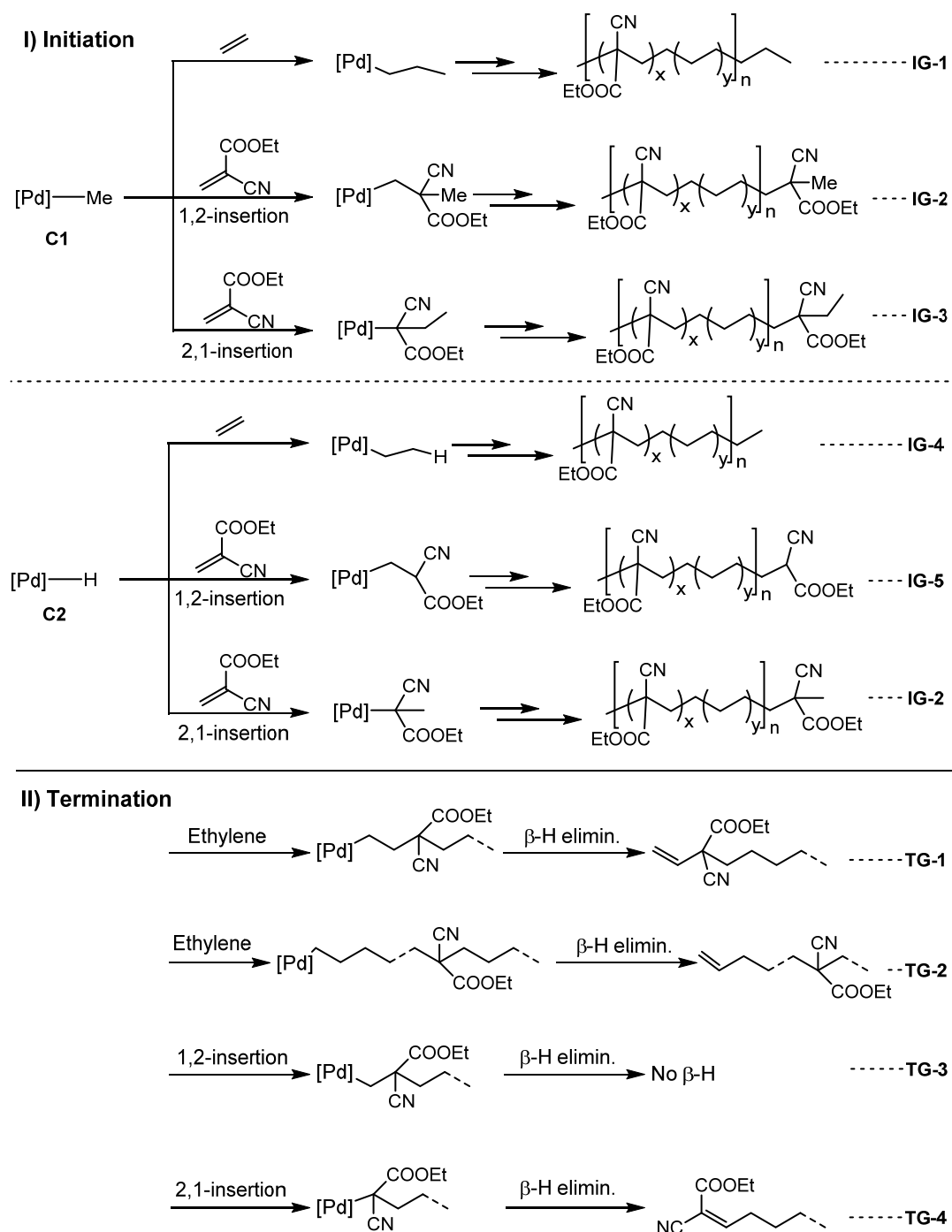


**Figure S41:** DSC thermogram (2<sup>nd</sup> heating cycle) of ET-ECA copolymer (Table S3, S3-5).

## 6. Proposed initiation and termination modes:

Potential initiation and termination mechanisms are depicted in scheme S1. The active species **C1** can undergo three different types of initiations to produce initiating-groups **IG-1**, **IG-2** and **IG-3**. The ethylene can coordinate and insert into Pd-Me bond to produce the initiating group **IG-1**. Careful analysis of the high temperature <sup>13</sup>C NMR data suggested presence of **IG-1** (Chart 2). Similarly, the functional olefin (Ethyl-2-cyanoacrylate = ECA) can coordinate and insert via 1,2-insertion mode or 2,1-insertion mode to generate **IG-2** and **IG-3** respectively. As outlined in scheme S1, **IG-2** can be potentially generated via 1,2-insertion of ECA in **C1** or via 2,1-insertion of ECA in **C2**. Irrespective of the origin of this group, <sup>13</sup>C NMR data suggested presence of **IG-2**. The 2,1-insertion product **IG-3** was also detected by <sup>13</sup>C NMR spectroscopy. In addition to these initiating modes, *in-situ* (after β-H elimination or transfer) generated [Pd]-H (**C2**) can also initiate the insertion polymerization. Thus, insertion of ethylene in [Pd]-H bond would produce **IG-4**.



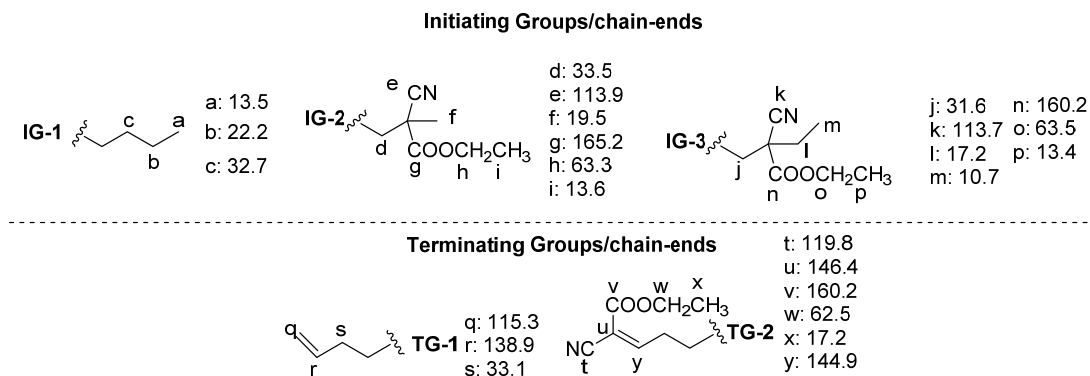


**Scheme S1:** Potential initiation and termination modes of ECA-ethylene copolymerization

1,2-insertion of functional olefin can result into **IG-5**; whereas 2,1-insertion of ECA will generate the initiating group **IG-2**.

The termination modes can vary in a wide range; however the most probable modes are presented in scheme S1. After a sequence of ethylene insertion, ECA can be inserted, which will be followed by ethylene insertion and  $\beta$ -H elimination. This sequence of insertion will result

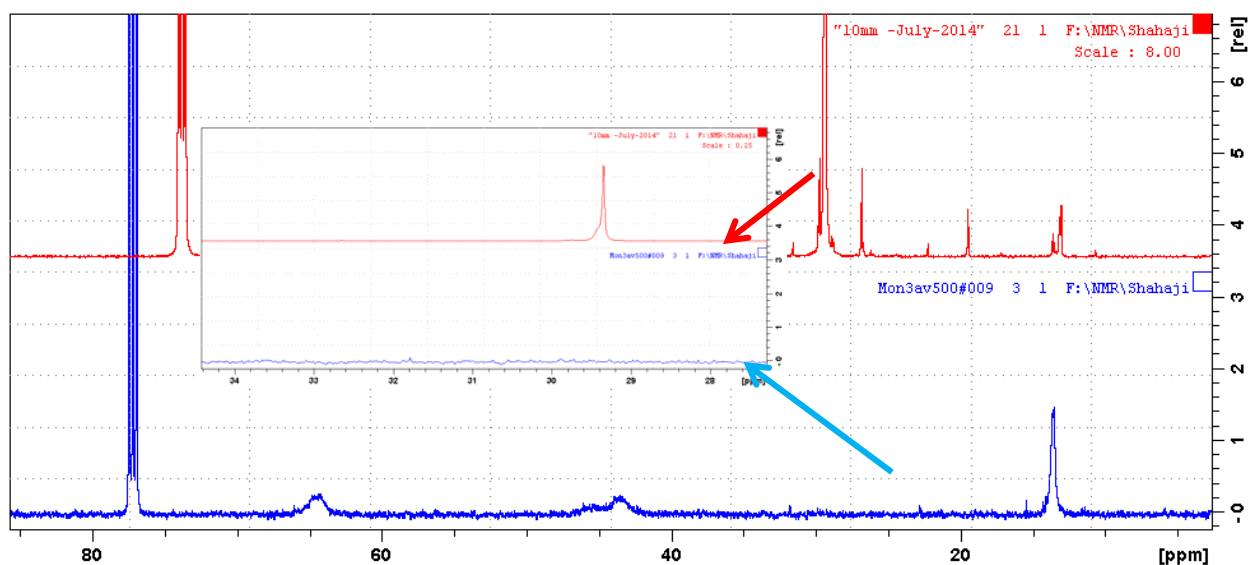
into the production of **TG-1** end group. The **TG-2** type chain ends are anticipated after multiple ethylene insertion and  $\beta$ -H elimination. Next, the growing polymer chain can be terminated immediately after ECA insertion. Multiple ethylene insertions, followed by 1,2-insertion (ECA) will generate a species without  $\beta$ -hydrogen; reducing the risk of termination via  $\beta$ -H elimination. In this case, termination by transfer is proposed. Termination after 2,1-insertion of ECA can produce **TG-4** chain ends.



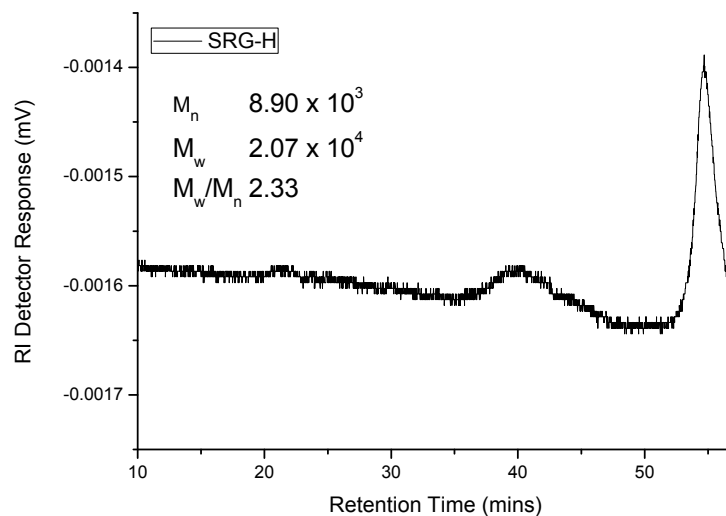
**Chart 2:** Potential initiating and terminating groups with  $^{13}\text{C}$  chemical shifts.

## 7. Control experiments:

**7.1 Ethylene-ECA polymerization without catalyst (3):** ECA is known to homopolymerize even in presence of traces of moisture and it is really difficult to avoid such ECA homopolymerization. As a control experiment, we investigated ECA-ethylene copolymerization in absence of catalyst **3**. Exactly same polymerization protocol as in section 4 (5 bar ethylene pressure, 0.06 mol/L ECA, 95°C for 1hr in presence of 35 mg of BHT) was followed, except that the catalyst (i.e. complex **3**) was not added to the reactor. This protocol led to the production of gel like material, which was dried and analyzed. The thus obtained polymer was found to be completely soluble in chloroform at room temperature. Hence, the  $^{13}\text{C}$  NMR of above polymer was recorded in  $\text{CDCl}_3$  at room temperature. Figure S42A depicts the comparison of copolymer obtained in run S3-4 (table S3) (top) and the homopolymer (bottom) obtained in this (control) experiment. As it is evident, no  $^{13}\text{C}$  resonance could be observed in the typical polyethylene region (between 28-34 ppm) in control experiment sample, whereas 29.3 ppm was the major resonance in copolymer sample (from run S3-4). Thus, absence of a matching carbon resonance at 29.3 ppm rules out formation ethylene-ECA copolymer in absence of catalyst **3**.



**Figure S42A:**  $^{13}\text{C}$  NMR of ET-ECA copolymer (Table S3, S3-4) in  $\text{C}_2\text{D}_2\text{Cl}_4$  at 393K (top) and ECA homopolymer in absence of complex **3** in  $\text{CDCl}_3$  at room 298K (bottom).

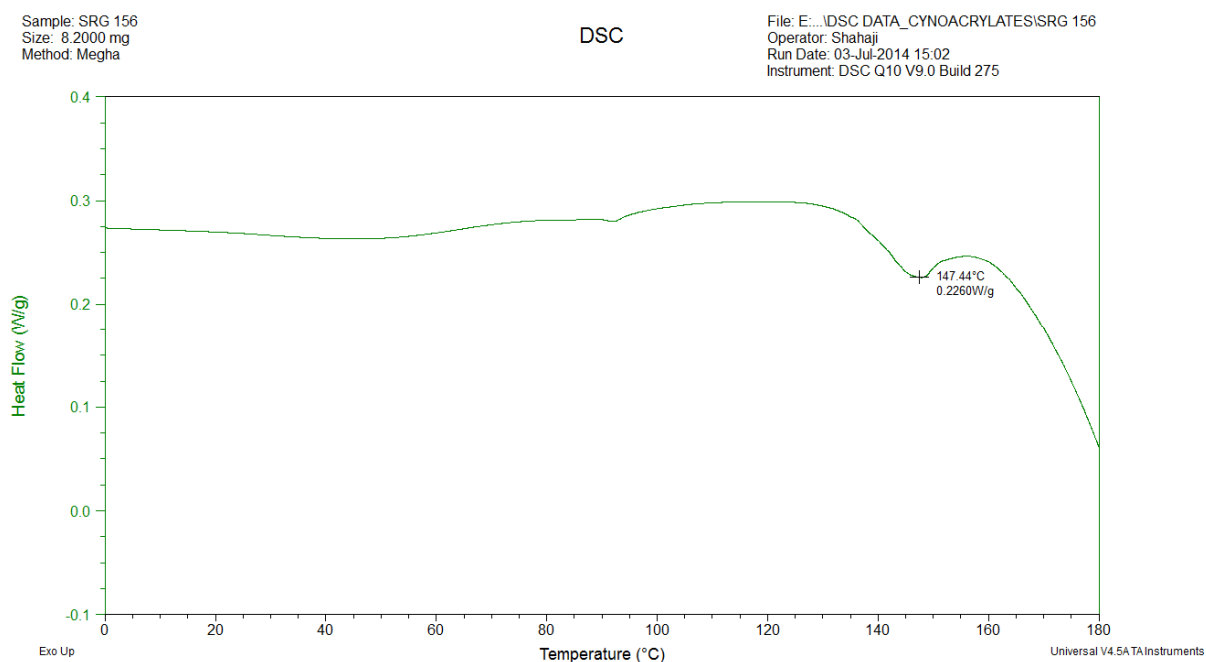


**Figure S42B:** GPC chromatogram of ECA homopolymer in chloroform at 25°C.

## 7.2 Evaluating existence of ECA homopolymer in the copolymer (from run S3-4):

Apart from the direct evidence presented in section 5.1 and 5.2; our hypothesis that ECA is incorporated in the polymer chain was further supported by the following control experiments.

- 1) The DSC scan of the ECA homopolymer (prepared as described in section 7.1) displayed a peak at 147°C (Fig. S43).<sup>6</sup> whereas, the copolymer sample from run S3-4 displayed a single peak at 123.6°C (Fig. S44) and no peak at 147°C could be detected. In addition to this, we prepared a physical mixture of 93 mg of neat polyethylene (that was prepared using complex **3**) and 7 mg of neat ECA homopolymer and analyzed it by DSC. The physical mixture clearly displayed two peaks, one at 126°C and another at 146°C (Fig. S45). These peaks can be easily ascribed to the PE and ECA homopolymer respectively. Thus, appearance of a single peak at 123.6°C and absence of 147°C peak in the copolymer sample (derived from run S3-4) clearly rules out the presence of ECA homopolymer and suggests incorporation of ECA in the copolymer.

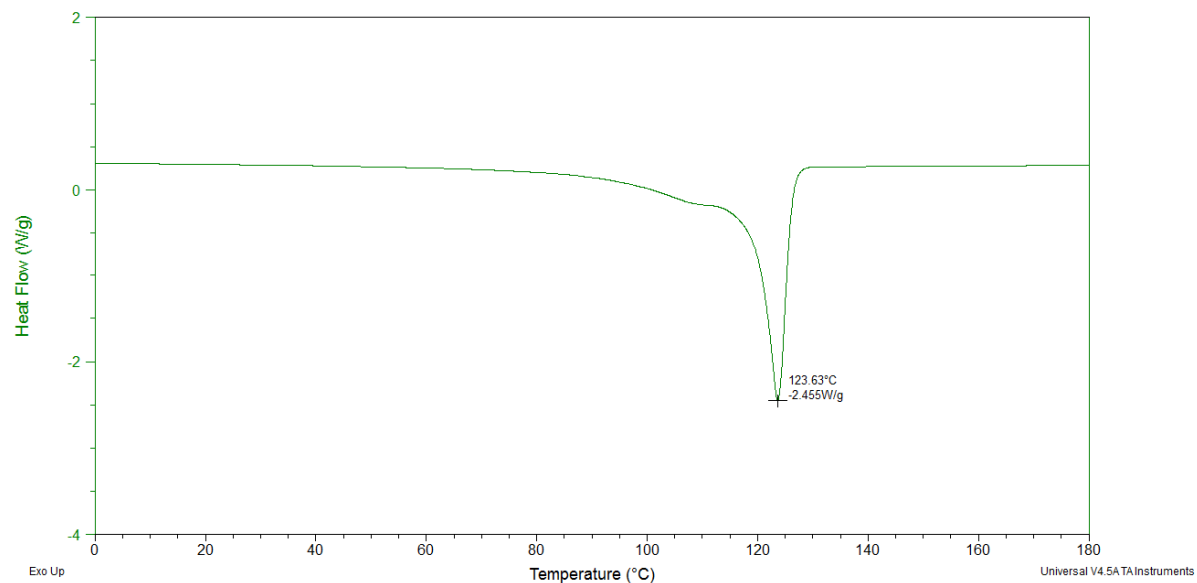


**Figure S43:** DSC thermogram of ECA-homopolymer.

Sample: srg\_164R11  
Size: 3.7000 mg  
Method: Megha

DSC

File: E:\New folder\srg\_164R2  
Operator: shahaji  
Run Date: 22-Aug-2014 14:08  
Instrument: DSC Q10 V9.0 Build 275

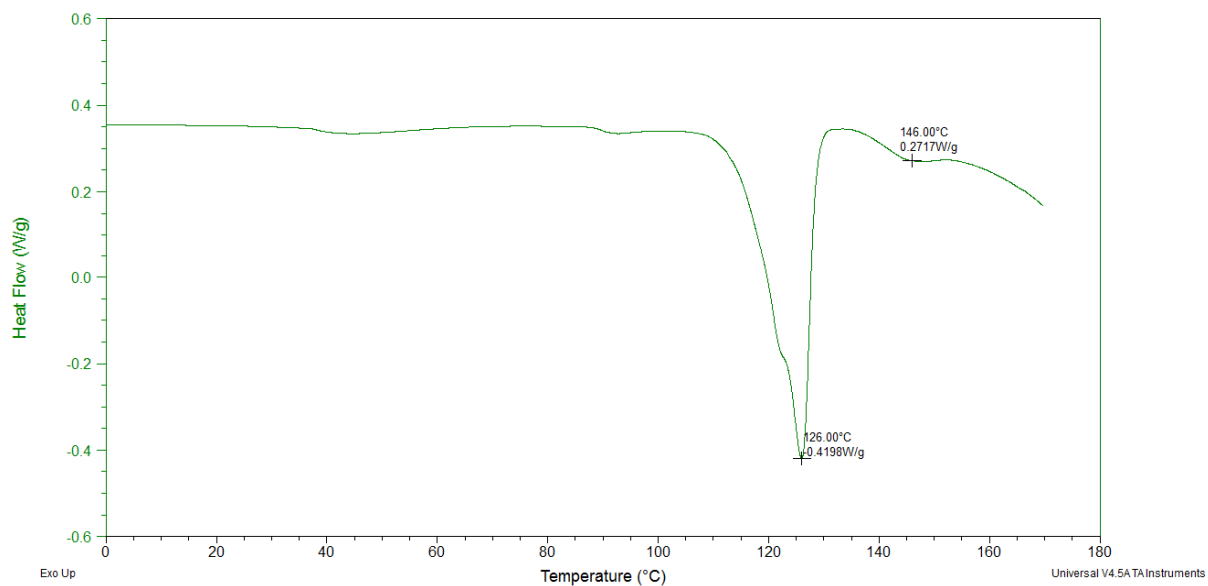


**Figure S44:** DSC thermogram (2<sup>nd</sup> heating cycle) of ET-ECA copolymer (Table S3, S3-4).

Sample: SRG-134+92  
Size: 6.2000 mg  
Method: SHAHAJI

DSC

File: E:\aug 2014\srg-134\SRG-134+92  
Operator: shahaji  
Run Date: 08-Jul-2014 20:26  
Instrument: DSC Q10 V9.0 Build 275

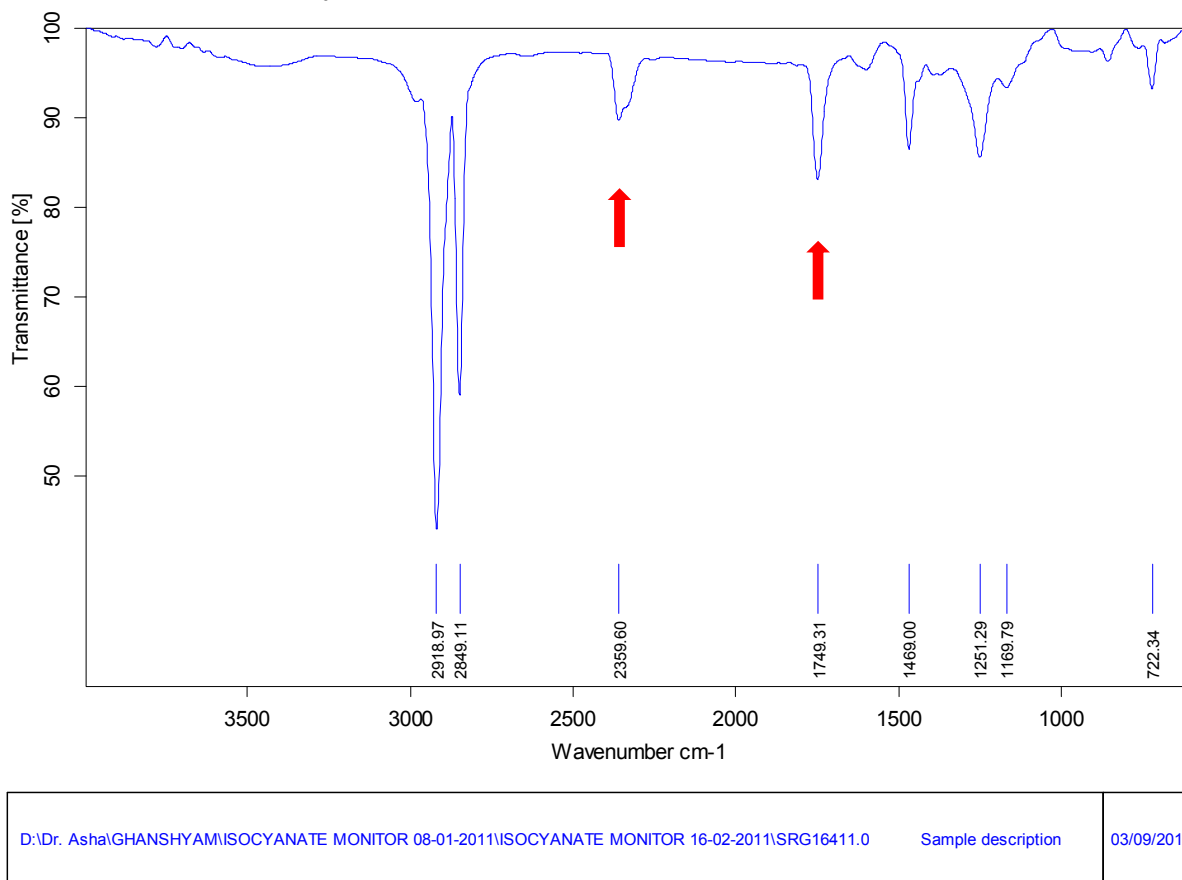


**Figure S45:** DSC thermogram of a physical mixture of polyethylene + ECA-homopolymer.

### 7.3 Existence of ET-ECA copolymer:

As described in section 4, the material obtained after polymerization was thoroughly washed with chloroform (3 times) and the NMR was recorded. The high temperature NMR investigation indicated incorporation of ECA, and the data has been presented in table S3. Our intensified efforts and control experiment as under, rule out the existence of homopolymer of ECA in the ethylene-ECA copolymer.

- 1) The copolymer sample in run S3-4 (table S3) was dissolved in trichlorobenzene (TCB) at 160°C and was re-precipitated by adding methanol. The precipitate was dried and IR spectrum was recorded. The infrared spectrum revealed existence of CN vibration band at 2359  $\text{cm}^{-1}$  and C-O stretching band at 1749  $\text{cm}^{-1}$ , indicating the incorporation of ECA in the re-precipitated copolymer sample.



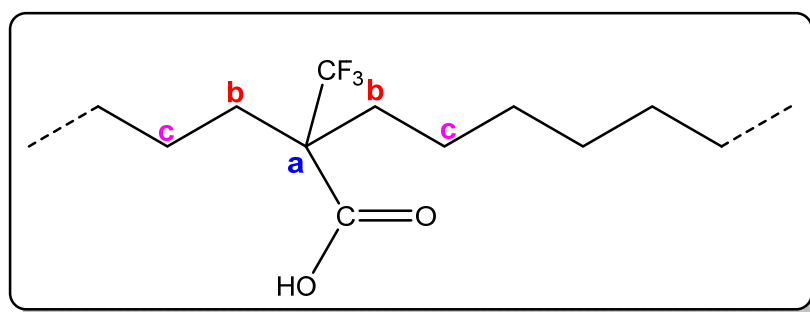
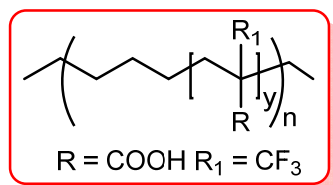
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**Figure S46:** Infrared spectrum of re-precipitated copolymer.

- 2) Similarly, the copolymer sample with highest incorporation (table S3 run S3-4) was suspended in chloroform for 48 hours at room temperature. After 48 hours, the turbid solution was filtered and the solid obtained was dried in vacuum. IR spectrum of the dried copolymer displayed CN and CO (2359  $\text{cm}^{-1}$  and 1749  $\text{cm}^{-1}$  respectively) bands, confirming the incorporation of ECA in the ethylene-ECA copolymer.

## 8. Copolymerization of ethylene-trifluoromethyl acrylic acid:

The ethylene-trifluoromethyl acrylic acid (TFMAA) copolymerization was carried out in a 50 ml glass high pressure reactor (Buechi-Mini clave) equipped with mechanical stirrer and heating/cooling jacket. Prior to the experiment, the reactor was heated in vacuum to 80°C for 30 minutes, cooled to room temperature and was filled with argon. Reactor was flushed with ethylene (3 times, 5-10 bars) and was charged with appropriate quantity of toluene under positive ethylene stream. Next, the reactor was pressurized to appropriate ethylene pressure (1 bar) and saturated with ethylene for 30 minutes at desired reaction temperature before it was cooled to room temperature. A solution of butylated hydroxyl toluene (37 mg, 0.16 mmol in 1 ml toluene), calculated amount of trifluoromethyl acrylic acid (diluted in 1 ml toluene) and catalyst solution (3:



12 mg, 20  $\mu\text{mol}$  in 5 ml DCM) was introduced into the reactor at room temperature. The reactor was then pressurized to desired ethylene pressure (1 bar) with stirring and appropriate temperature (95°C) was reached within 1-5 minutes.

The polymerization was generally carried out for 60 minutes, the excess ethylene was slowly vented off and the reactor was allowed to cool down to room temperature under argon. The resultant solution was transferred to a Schlenk flask with syringe and the volatiles were evaporated in vacuum to obtain solid mass. The thus obtained solid material was washed thrice with diethyl-ether (3  $\times$  10 mL) and the insoluble solid was dried under reduced pressure for 4 hours. The insoluble copolymer fraction was thoroughly investigated using a combination of spectroscopic and analytical tools and the results are summarized in table S5. A proton resonance at 2.1 ppm can be ascribed to methylene protons in the copolymer back-bone (Fig. S47).<sup>8</sup> Furthermore, absence of characteristic proton resonance at 3.4 ppm ruled out the presence of TFMAA homopolymer (ESI S50). In addition, no TFMAA homopolymer could be obtained in a blank run without catalyst. A <sup>19</sup>F NMR spectrum (S51) of the oligomeric fraction (accessed by suspending the copolymer in excess chloroform) revealed characteristic signals at -65.1, -66.1, -66.7 and -68.4 ppm. These chemical shifts are similar to those reported for ethylene-trifluoropropene copolymers (the closest copolymer known) and can be readily assigned to ET-TFMAA oligomers. Absence of characteristic splitting pattern and signal broadening hampered further analysis and the peaks can be tentatively assigned to structures A, B, C, D. An IR spectrum of the copolymer revealed a characteristic  $\nu$  (C=O) at 1710  $\text{cm}^{-1}$  (Fig. S49), that can be ascribed to acidic CO and is in line with earlier reports.<sup>9</sup> Furthermore, a typical -OH band was observed at 3368  $\text{cm}^{-1}$ , which, together with CO band indicates the existence carboxylic group in the copolymer. MALDI-ToF-MS spectrum of the copolymer also indicated TFMAA incorporation and various copolymer fragments could be identified (see table S6 and fig. S52A-C).

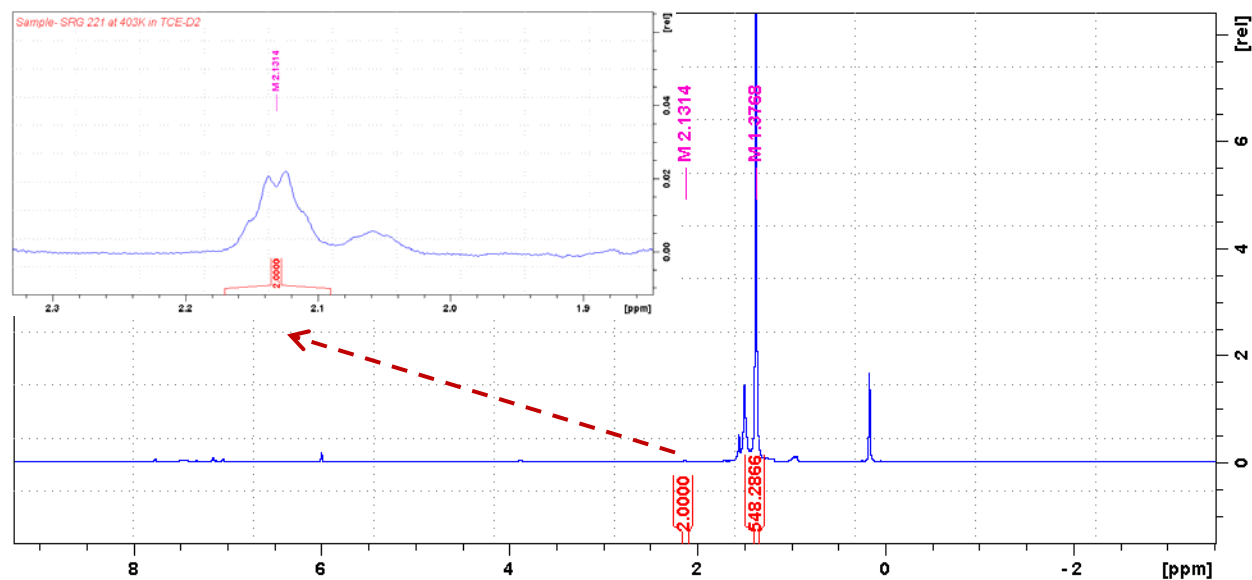
$^1\text{H}$  NMR (500 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 403 K):  $\delta$  = 2.1 (br., m,  $\text{H}_\text{b}$ ), 1.37 (br., s,  $\text{H}_\text{c}$ ).

**Table S5:** Copolymerization of ethylene–trifluoromethyl acrylic acid in presence of complex **3**<sup>a</sup>

Run	TFMAA(mol/L)	$\text{C}_2\text{H}_4$ (bar)	% Incorp. <sup>b</sup>	Yield (g)	$M_n$ ( $10^3$ g/mol) <sup>c</sup>	$M_w/M_n$ <sup>c</sup>
S5-1	0.06	1	0.73	0.37	ND	ND
S5-2 <sup>d</sup>	3.0	1	3.0	0.07	2.8	1.2

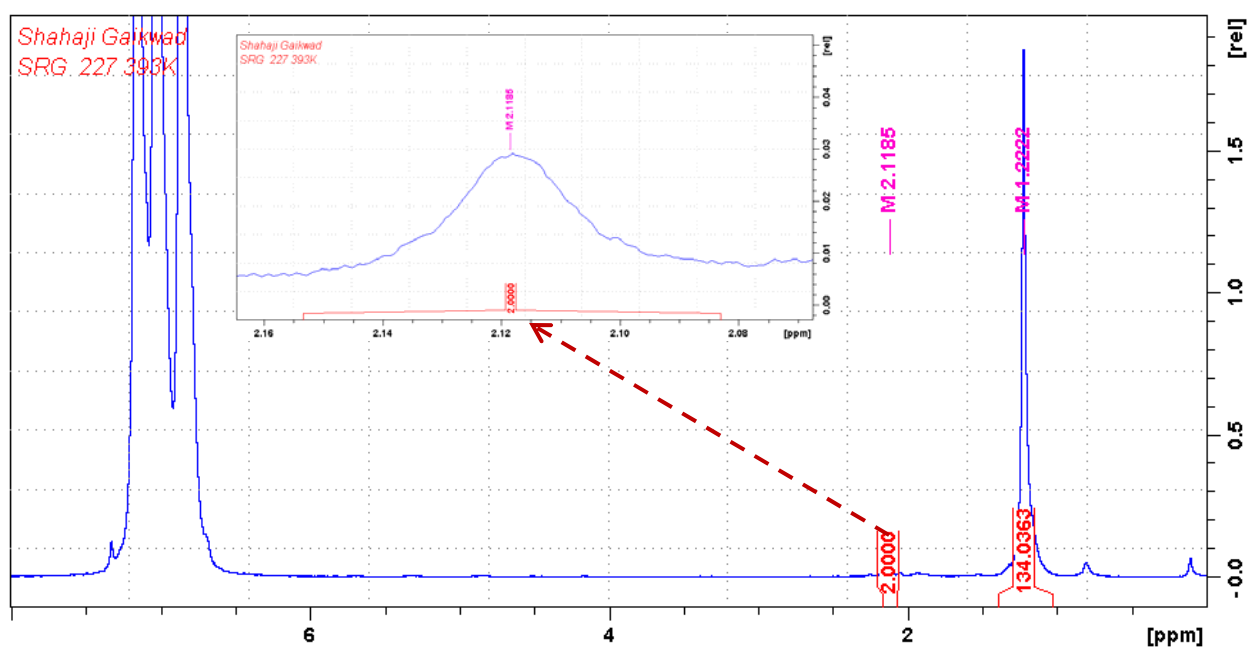
<sup>a</sup>Reaction conditions: **3** = 20  $\mu\text{mol}$  in DCM, toluene = 50 ml (Toluene + TFMAA); temperature = 95°C, time = 1 hour,

<sup>b</sup>TFMAA incorporation was determined by high temperature  $^1\text{H}$  NMR in  $\text{C}_2\text{D}_2\text{Cl}_4$  at 130°C; <sup>c</sup>Determined by high temperature GPC at 160°C in tri-chlorobenzene against PS standard; <sup>d</sup>TFMAA incorporation was determined by high temperature  $^1\text{H}$  NMR in  $\text{C}_6\text{D}_6$ +TCB (10:90) mixture at 120°C.

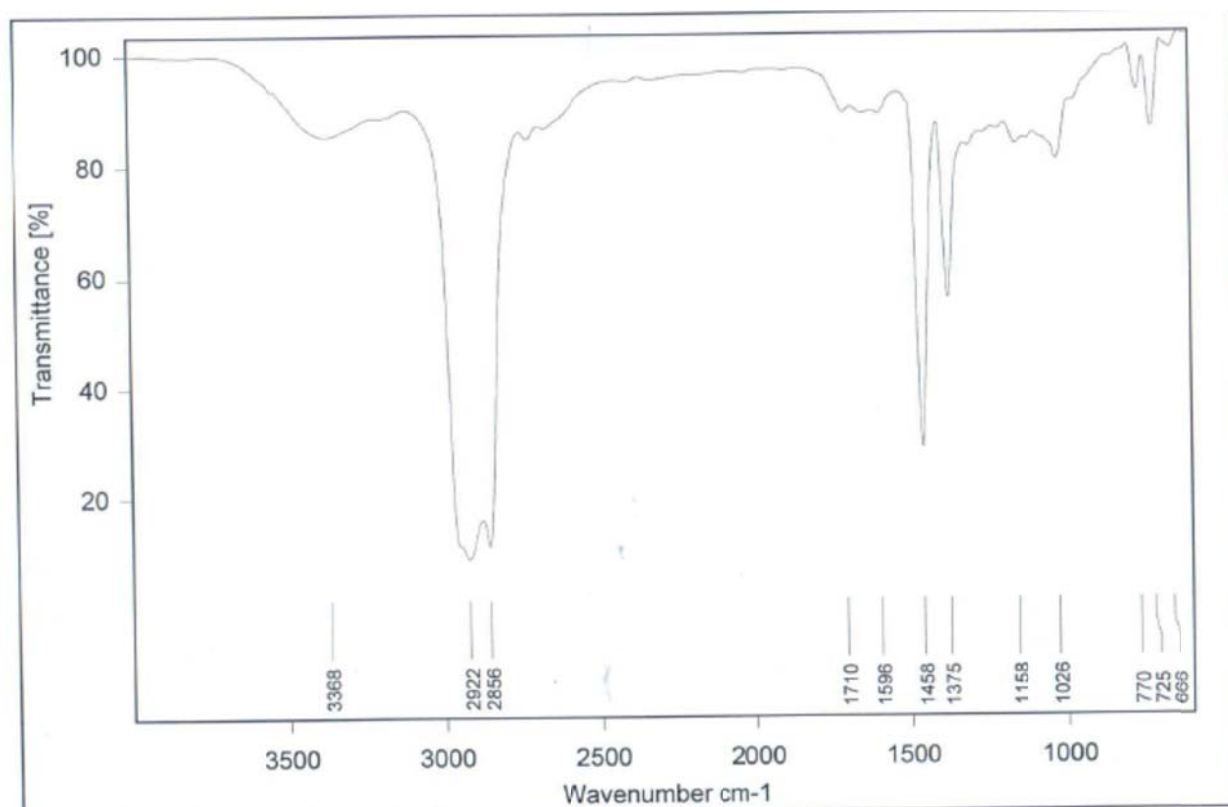


**Figure S47:**  $^1\text{H}$  NMR of ET-TFMAA copolymer in  $\text{C}_2\text{D}_2\text{Cl}_4$  at 403K (Table S5, run S5-1).

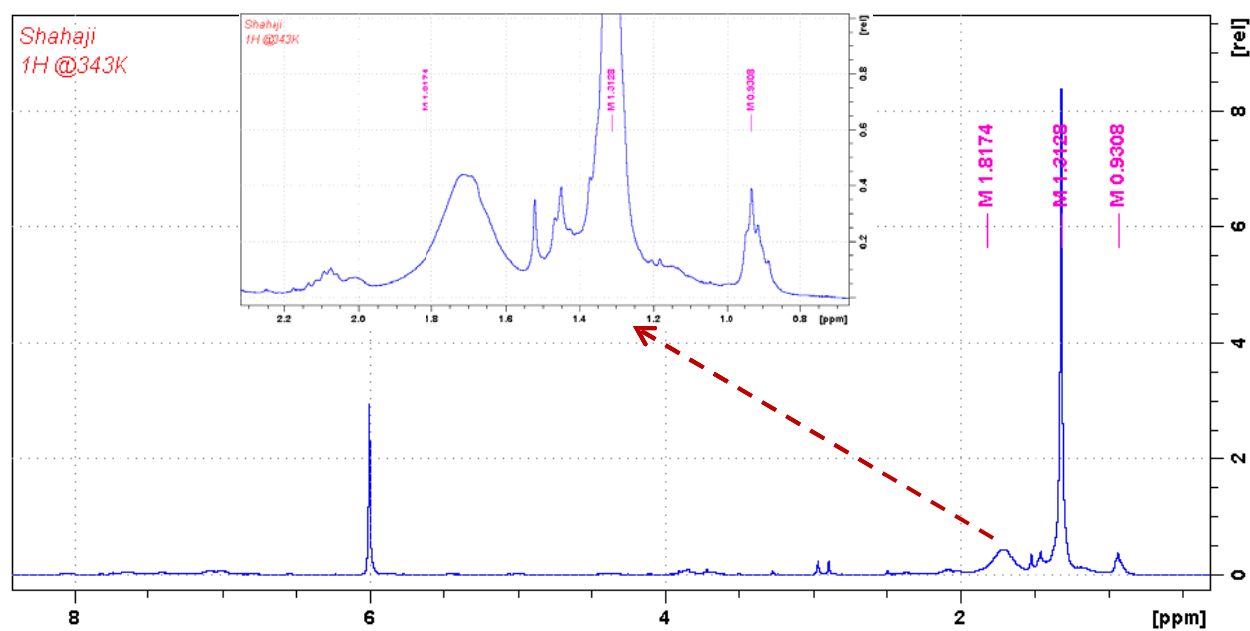




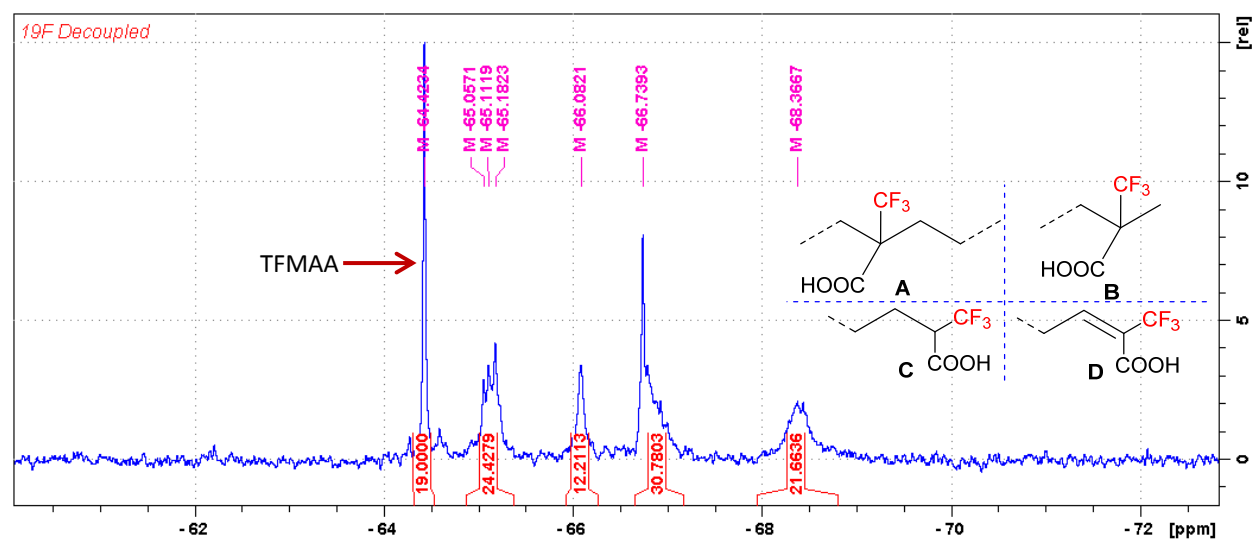
**Figure S48:**  $^1\text{H}$  NMR of ET-TFMAA copolymer in TCB+C<sub>6</sub>D<sub>6</sub> at 393K (Table S5, run S5-2).



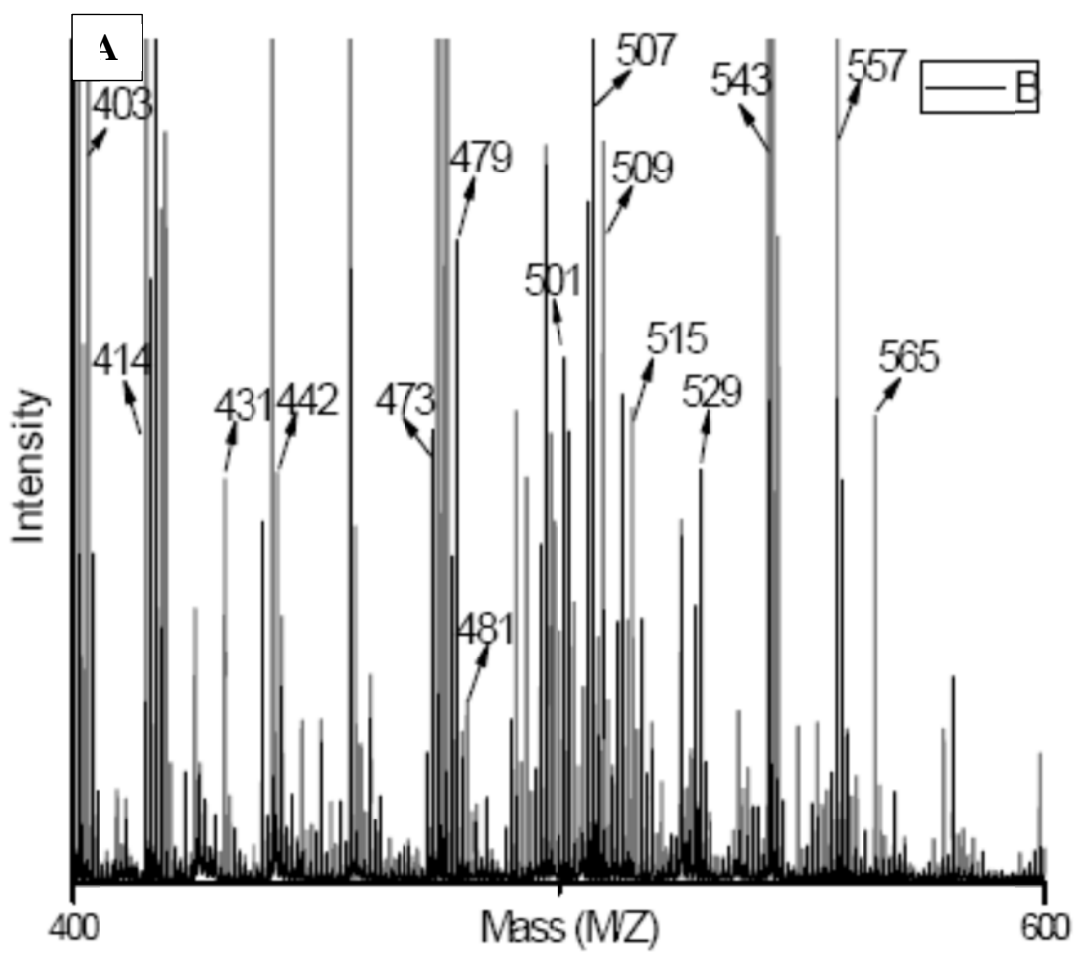
**Figure S49:** IR spectrum of ET-TFMAA copolymer (Table S5, run S5-2).

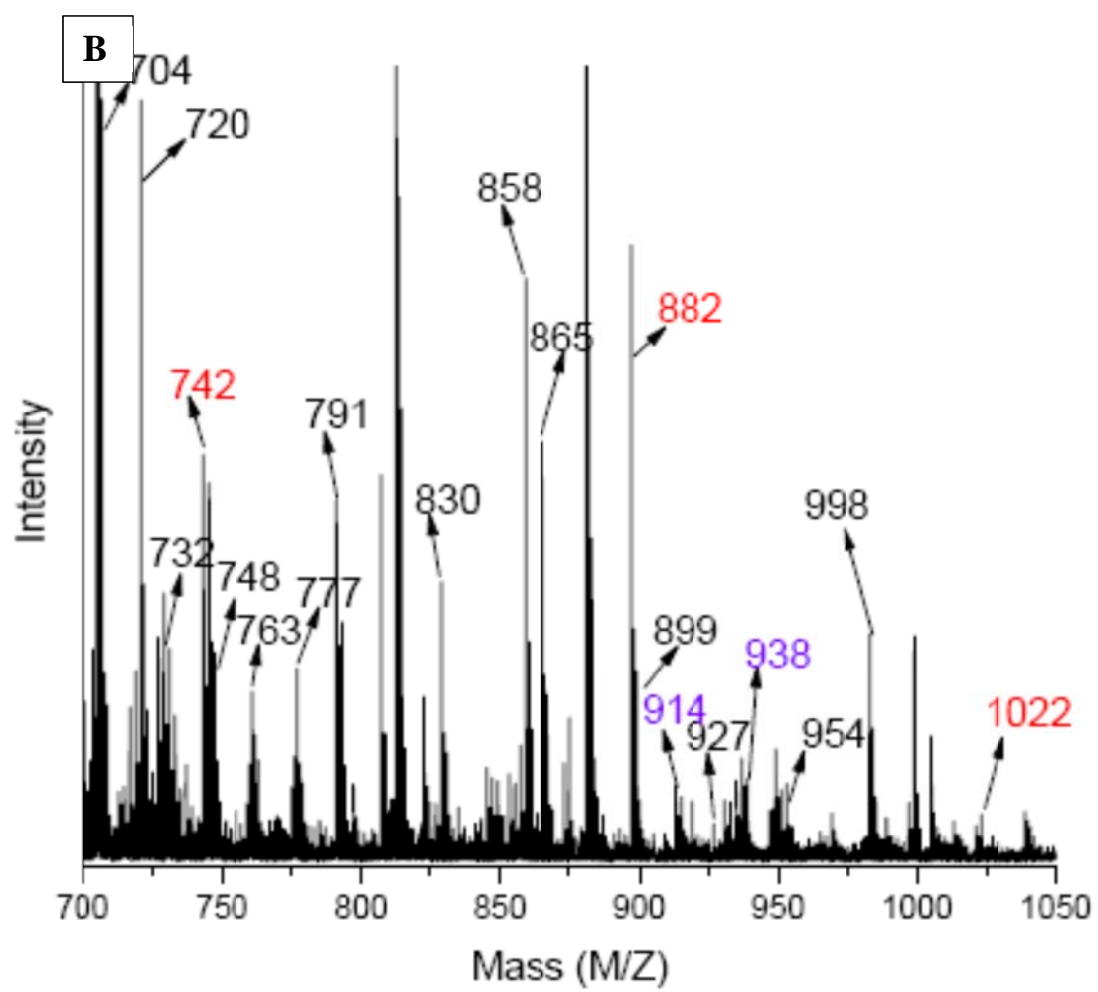


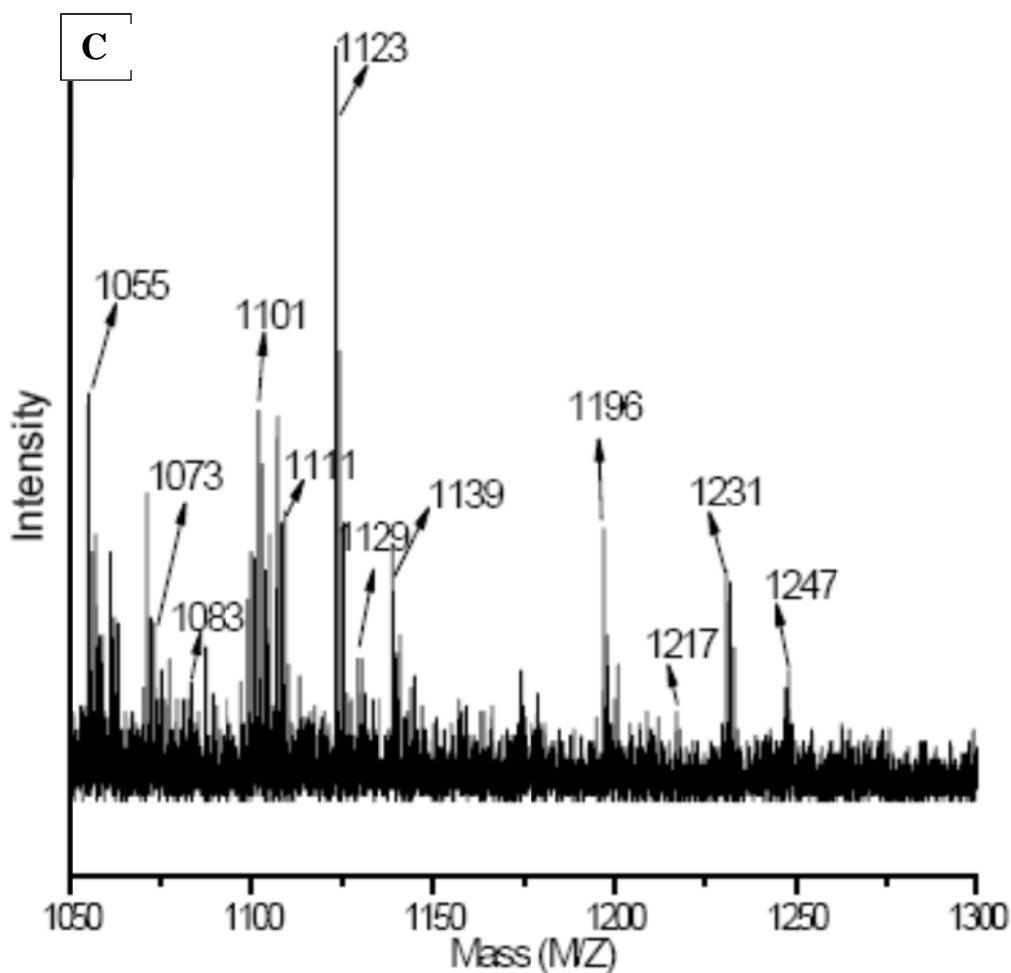
**Figure S50:** <sup>1</sup>H NMR of chloroform soluble low molecular weight oligomeric fraction (extracted from copolymer obtained in run S5-2) in C<sub>2</sub>D<sub>2</sub>Cl<sub>2</sub> at 343K.



**Figure S51:**  $^{19}\text{F}$  NMR ( $^1\text{H}$  decoupled) of chloroform soluble low molecular weight oligomeric fraction (extracted from copolymer obtained in run S5-2) in  $\text{C}_2\text{D}_2\text{Cl}_2$  at 343K.







**Figure S52A-C:** MALDI-ToF-MS spectra of a copolymer of ethylene and trifluoro-methyl acrylic acid (table S5, run S5-2).

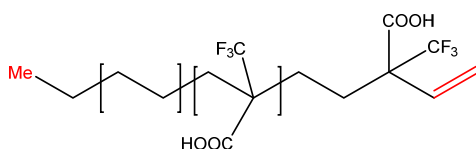
**Table S6:** MALDI-ToF-MS of copolymer of ethylene–trifluoromethyl acrylic acid; CET<sub>x</sub>TFMAA<sub>y</sub> indicates a copolymer chain of “x” ethylene units and “y” trifluoromethyl-acrylic acid units initiated by Pd-Me group. Similarly, HET<sub>x</sub>ECA<sub>y</sub> indicates a copolymer chain initiated by Pd-hydride group. The following peaks were identified from a set of probabilities reported in table S7.

<i>m/z</i>	<i>Copolymer</i>
518	CET <sub>8</sub> TFMAA <sub>2</sub>
546	CET <sub>9</sub> TFMAA <sub>2</sub>
742	CET <sub>6</sub> TFMAA <sub>4</sub>
882	CET <sub>6</sub> TFMAA <sub>5</sub>

938	CET <sub>8</sub> TFMAA <sub>5</sub>
1022	CET <sub>6</sub> TFMAA <sub>6</sub>
1246	CET <sub>9</sub> TFMAA <sub>7</sub>

Apart from the fragments reported in above table, many peaks with a mass difference of 28 or multiples of 28 were detected (see fig.S52A).

**Table S7:** Ethylene and trifluoromethyl acrylic acid permutations and combinations with olefin insertion in a Pd-Me bond.



<i>n</i>	<i>CET<sub>n</sub>TF MAA</i>	<i>CET<sub>n</sub>TFM AA2</i>	<i>CET<sub>n</sub>TFM AA3</i>	<i>CET<sub>n</sub>TFM AA4</i>	<i>CET<sub>n</sub>TFM AA5</i>	<i>CET<sub>n</sub>TFM AA6</i>	<i>CET<sub>n</sub>TFM AA7</i>
4	266	406	546	686	826	966	1106
5	294	434	574	714	854	994	1134
6	322	462	602	742	882	1022	1162
7	350	490	630	770	910	1050	1190
8	378	518	658	798	938	1078	1218
9	406	546	686	826	966	1106	1246
10	434	574	714	854	994	1134	1274
11	462	602	742	882	1022	1162	1302
12	490	630	770	910	1050	1190	1330
13	518	658	798	938	1078	1218	1358
14	546	686	826	966	1106	1246	1386
15	574	714	854	994	1134	1274	1414
16	602	742	882	1022	1162	1302	1442
17	630	770	910	1050	1190	1330	1470
18	658	798	938	1078	1218	1358	1498
19	686	826	966	1106	1246	1386	1526
20	714	854	994	1134	1274	1414	1554

21	742	882	1022	1162	1302	1442	1582
22	770	910	1050	1190	1330	1470	1610
23	798	938	1078	1218	1358	1498	1638
24	826	966	1104	1246	1386	1526	1666
25	854	994	1132	1274	1414	1554	1694
26	882	1022	1160	1302	1442	1582	1722
27	910	1050	1188	1330	1470	1610	1750
28	938	1078	1216	1358	1498	1638	1778
29	966	1106	1244	1386	1526	1666	1806
30	994	1134	1272	1414	1554	1694	1834
31	1022	1162	1300	1442	1582	1722	1862
32	1050	1190	1328	1470	1610	1750	1890
33	1078	1218	1356	1498	1638	1778	1918
34	1106	1246	1384	1526	1666	1806	1946
35	1134	1274	1412	1554	1694	1834	1974
36	1162	1302	1440	1582	1722	1862	2002
37	1190	1330	1468	1610	1750	1890	2030
38	1218	1358	1496	1638	1778	1918	2058
39	1246	1386	1524	1666	1806	1976	2086
40	1274	1414	1552	1694	1834	1974	2114

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