Electronic Supplementary Material (ESI) for Chemical Science.

Supporting information

Controlled living anionic polymerization of cyanoacrylates by frustrated Lewis pair based initiators

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Table of Contents

This section includes detailed information related to the experimental conditions, devices, methods and procedures. It also collects MS and NMR spectra as well as GPC traces and calorimetric traces resulting from analysis that could be relevant to support the discussions in the article.

1.-Devices, Methods and Procedures

1.1.- Devices and methods:

- Gel Permeation Chromatography (UAB – Barcelona):
  Agilent 1260 Infinity (degas, pump, automatic injector, RI detector)
  PL gel guard column, 5 µm, 50 x 7.5 mm
  PL Mixed gel C, 5 µm, MW 200-3M, 300 x 7.5 mm
  PL gel 5 µm, 10^4 Å, 300 x 7.5 mm
  Solvent - THF; 1mL/min flow; 40 °C column temperature
  Calibration standards: PMMA
- Gel Permeation Chromatography (Henkel – Dublin):
  Agilent 1260 Infinity (degas, pump, automatic injector, RI detector)
  PL gel guard column, 5 µm, 50 x 7.5 mm
  PL Mixed gel C, 5 µm, MW 200-300,000M, 300 x 7.5 mm
  PL gel 5 µm, 10^4 Å, 300 x 7.5 mm
  Solvent - Dichloromethane; 1 mL/min flow; 40°C column temperature
  Calibration standards: PMMA
- NMR (*Servei de Ressonància Magnètica Nuclear* at UAB):
  Bruker DRX-250 MHz; Bruker AVANCE-III 400 MHz. All chemical shifts are given in ppm (δ).
- Drying system (UAB – Barcelona):
  Innovative Technology PS-MD-2 (source of THF before drying protocol)
- Dry glove box (UAB - Barcelona):
  MBraun UniLab 9550
- Calorimeter (Henkel – Dublin):
  TC 08 Thermocouple data logger (PICO Technology)
  Thermocouple type K 4.5 mm
- MALDI-TOF MS (CSIC –Zaragoza):
  Bruker BIFLEX (Brucker-Franzen Analityk) Modus Reflection
  Laser wavelength: 337 nm
  Laser voltage: 19 kV
  Matrix: *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene] malonitrile (DCTB)

1.2.- Procedures

The following paragraphs describe the experimental procedures that have been followed for most of the activities involved in this research. Notice that in some occasions

there are only small differences between different procedures, and so they are always referred to the most similar one highlighting the variations.

1.2.1.- Drying - purifying:

- Argon, nitrogen and hydrogen:

High purity gas from the bottle was passed through a column filled with several drying agents: calcium chloride, phosphorus pentoxide and molecular sieves, with a layer of silica-cobalt indicator to assure no water presence at the end of the column.

- Tetrahydrofuran (THF), hexane, toluene:

200 mL of high purity solvent were placed in a 250 mL flask coupled to a reflux distillation collector system refrigerated by cold water. Pure sodium pieces were added to the solvent as drying agent and a small amount of benzophenone was incorporated as indicator. A magnetic stirring bar was placed in the flask to assure a constant and homogeneous boiling and a current of nitrogen or argon was passed through the system to avoid air presence. The solvent was kept under reflux in these conditions until the solution reached a dark blue-purple color that indicated no water presence. Then the freshly distilled dry solvent was collected with a syringe, placed in a Schlenk flask under argon atmosphere and used for a given experiment or stored in a dry glove box.

- Tetramethylpiperidine (TMP):

5 mL of 98% pure TMP were placed in a flask under argon atmosphere with a magnetic bar and calcium hydride as drying agent. Then the TMP was heated at 130°C for 2 hours and finally distilled at 160°C and 1 atm., collected in a Schlenk flask under argon atmosphere and freshly used for $[TMPH^+][HB(C_6F_5)_3^-]$ synthesis.

- Monomers:

Monomers were always handled with LDPE transfer pipettes. The purifying protocol implied distillation under reduced pressure using pretreated acid washed glassware. 50 mL of monomer and a stir bar were placed in the distillation flask. The system was then closed and taken to 10^{-2} mbar under vigorous magnetic stirring. The temperature was then raised until distillation started. In order to avoid any damage in the vacuum pump two consecutive cold traps immersed in liquid nitrogen were placed between the collector flask and the pump. The first and last part of the distilled monomer were discarded, whereas the second third was collected and stored in a HDPE bottle under argon atmosphere at -30°C.

- Dry glassware:

All glassware is cleaned, flushed with acetone and dried in an oven for 4 hours at 130 °C before using it, trying to avoid water condensation from the air replacing it with argon when the material is cooling down.

When applicable, glassware was pretreated as follows: clean glassware flask and stirring bar were flushed with sulfuric acid 1M and dried for 4 hours at 130°C. Then they were flushed with acetone and dried again, repeating this acetone cleaning-drying cycle for three times.

1.2.2.-GPC sample preparation

1-10 mg of dry solid polymer (depending on the expected Mn) were placed in a vial and dissolved in 1 mL of THF. When completely dissolved the polymer solution was passed through a 2 μm porous filter and placed in a GPC vial for its analysis. An alternative method included the direct injection of the living polymer solution in the GPC. This preferred method kept always a concentration of 1 mg/mL in the injected sample.

1.2.3.-Synthesis of FLP based initiator $[TMPH^+][HB(C_6F_5)_3^-]$[1]

In a dry glove box under argon atmosphere, 0.9 g (1.67 mmol) of tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, were placed in a dry Schlenk flask provided with a dry magnetic stirring bar. Then 20 mL of dry toluene were added and magnetic

stirring was started. When $B(C_6F_5)_3$ was completely dissolved, 254 μL (1.5 mmol) of distilled 2,2,6,6-tetramethylpiperidine (TMP) were injected in the flask. The argon was then replaced by dry hydrogen at 1 atm of pressure and the solution was kept under these conditions for 2 hours. Then all volatiles were removed under reduced pressure to give a white solid that was recrystallized twice at room temperature in dry Toluene-Hexane 1:2 for 12 hours to give transparent cubic crystals. The crystals were then filtered off, cleaned with dry cold hexane, and placed again in a Schlenk flask. The flask was finally taken out of the dry glove box, and the pure crystals were dried under reduced pressure and stored under argon atmosphere. Yield: 0.75 g, 76,3%; Purity: 100%

1.2.4.-Polymerization procedures: optimization process

A) Experiments 1-6 (Table 1), 9-11 (Table 2) and Figure 1a:

0,056 mmol of initiator were placed at room temperature in a dry 50 mL flask glassware containing a stirring bar under dry argon atmosphere. Then 20 mL of dry THF were added and vigorously magnetic stirring was started. When the initiator was completely dissolved, 4.48 mmol of not purified CA monomer were added dropwise to start the polymerization. To analyze the polymeric species, 2.5 mL aliquots were withdrawn from the flask at the considered polymerization time using a syringe. The polymer was killed adding 0.5 mL of HCl 1M and all volatiles were removed under reduced pressure to give a white solid.

Experiments 1 and 6 of Table 1 were also tested with distilled monomer. In the case of BuLi, the amount of daughter polymer was reduced, but was still remains considerable. The experiment with PPh_3 was quite similar and not clear effect was observed. See GPC traces below. GPC trace of Figure 1a corresponds to experiment 1 with distilled monomer.

B) Experiments 1-8 (Table 2), and Figure 3(a):

1 mL of dry THF was placed in a propylene cup and vigorously stirred. Then a suitable amount of initiator solution was added to obtain a final concentration of initiator 0.0028 M. After that 34 μL of distilled monomer (0.224 M) were injected with the aid of a micropipette equipped with plastic precision tips to start the polymerization. The sequential additions (experiment in Figure 3(a)) were performed through injections of 34

μL of monomer in the same way than the previous one. To analyse the resulting 1st, 2nd and 3rd generation polymers, a suitable amount of polymer solution (to reach 1 mg/mL GPC sample) was transferred to a GPC vial containing a very slightly acidified solvent to ensure that the polymer species would not evolve.

C) Experiments in Figure (1b) and Figure 3(c-f):

A given molar amount of distilled monomer was added dropwise into 20 mL of THF at a given temperature in dry 50 mL flask glassware under vigorous stirring and dry argon/nitrogen atmosphere. Just after finishing the monomer addition a concentrated solution containing the initiator (1/80 of the given molar amount of monomer) was injected pushing quickly the syringe plunger. After 1 hour of reaction time, all volatiles were removed to obtain a white solid 1st generation polymer. This polymer was stored for 72 hours under dry argon atmosphere and further re-dissolved in THF. The second monomer addition was performed drop by drop over a solution containing the re-dissolved first generation polymer in THF, to form the 2nd generation polymer. The procedure was repeated until obtaining a 3rd generation poly(cyanoacrylate). To analyze the polymeric species, 2.5 mL aliquots were withdrawn from the flask using a syringe. The polymer was killed adding 0.5 mL of HCl 1M and the volatiles were removed under reduced pressure to give a white solid.

1.2.5.-Procedure for calorimetric studies an k_p estimation

The temperature was monitored with the time immersing a thermocouple type K (RS 397-1236) in the polymerization solution according to polymerization procedure (B) and then recording the data with the aid of a TC 08 Thermocouple data logger (PICO Technology). The obtained temperature values were translated to monomer conversion as follows:

$$T=T_0 \rightarrow [M]=[M]_0 \rightarrow t=0$$
$$T=T_f \rightarrow [M]=0 \rightarrow t=t_f$$

Were T_0 and T_f are initial and final temperatures and $[M]_0$ and [M] the free monomer concentration and time t=0 and $t=t_{final}$, respectively. The values are then represented according to 1st order kinetics $ln\frac{M_0}{M} = k_{ap}\cdot$ t and the propagation rate constant estimated by $k_{ap} = k_p \cdot [living\ ends]$, where [living ends] = constant = $[initiator]_0$.

2.-Analytical Supporting Material

This section collects analytical results from most of the performed experiments, which are relevant for the assumption of the conclusions depicted in the article.

2.1.-NMR Spectra of Synthesized $[TMPH^+][HB(C_6F_5)_3^-]$

^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 5.50 (br t, $^1J_{NH}$ = 51.0 Hz, 2H, NH_2), 3.43 (br q, $^1J_{BH}$ = 84.1 Hz, 1H, BH), 1.86 (m, 2H, CH_2), 1.78 (m, 4H, CH_2), 1.49 (s, 12H, CH3)

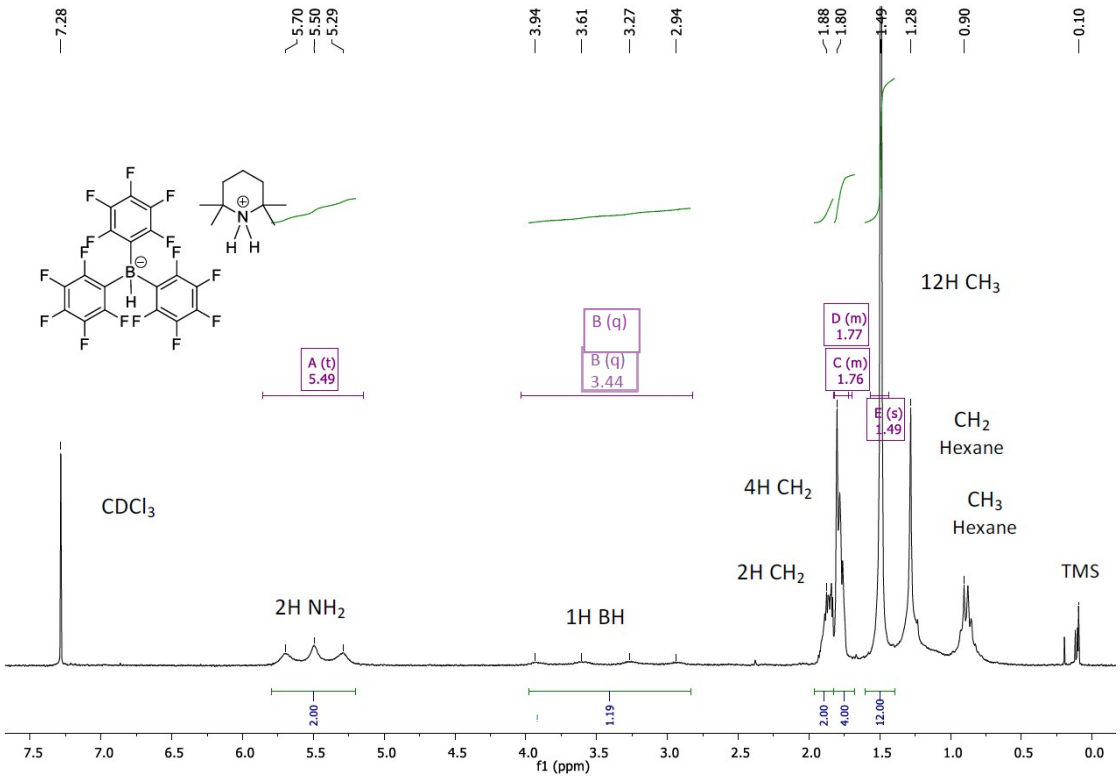

Figure S1.^1H NMR spectrum of $[TMPH^+][HB(C_6F_5)_3^-]$ (250 MHz, $CDCl_3$)

^{19}F NMR (235 MHz, $CDCl_3$) δ -134.17 (d, 6F, $^3J_{FF}$ = 22.4 Hz, ortho-C_6F_5), -161.96 (t, 3F, $^3J_{FF}$ = 20.3 Hz, para-C_6F_5), -165.82 (m, 6F, meta-C_6F_5)

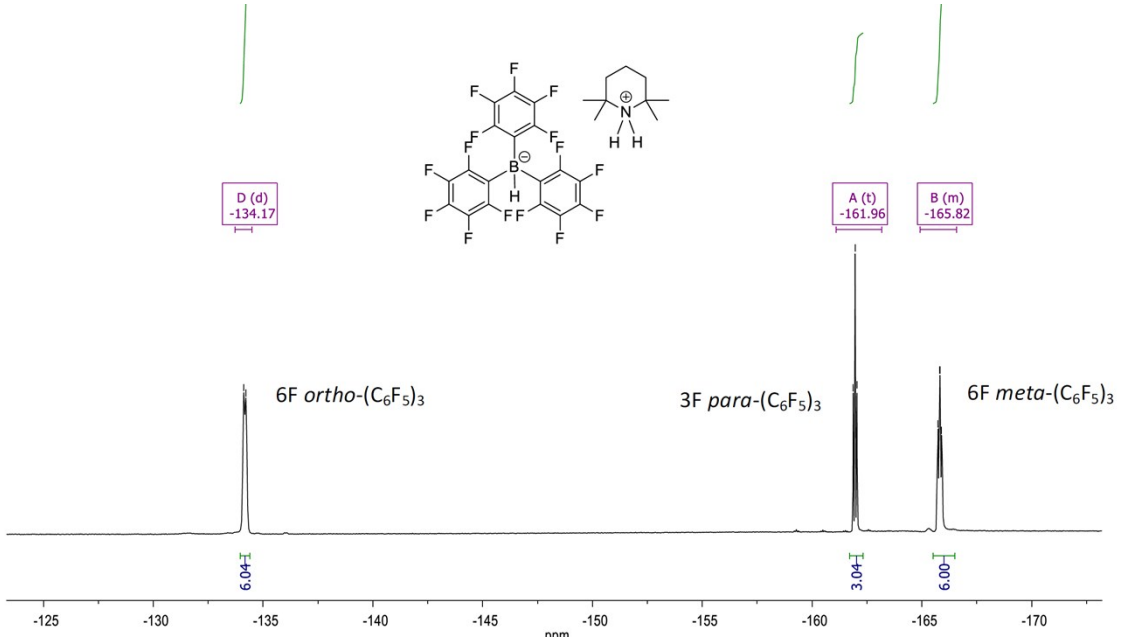

Figure S2. ^{19}F NMR spectrum of [TMPH$^+$][HB(C_6F_5)$_3^-$] (235 MHz, $CDCl_3$)

^{11}B NMR (128 MHz, $CDCl_3$) δ -24.48 (d, $^1J_{BH}$ = 84.1 Hz).

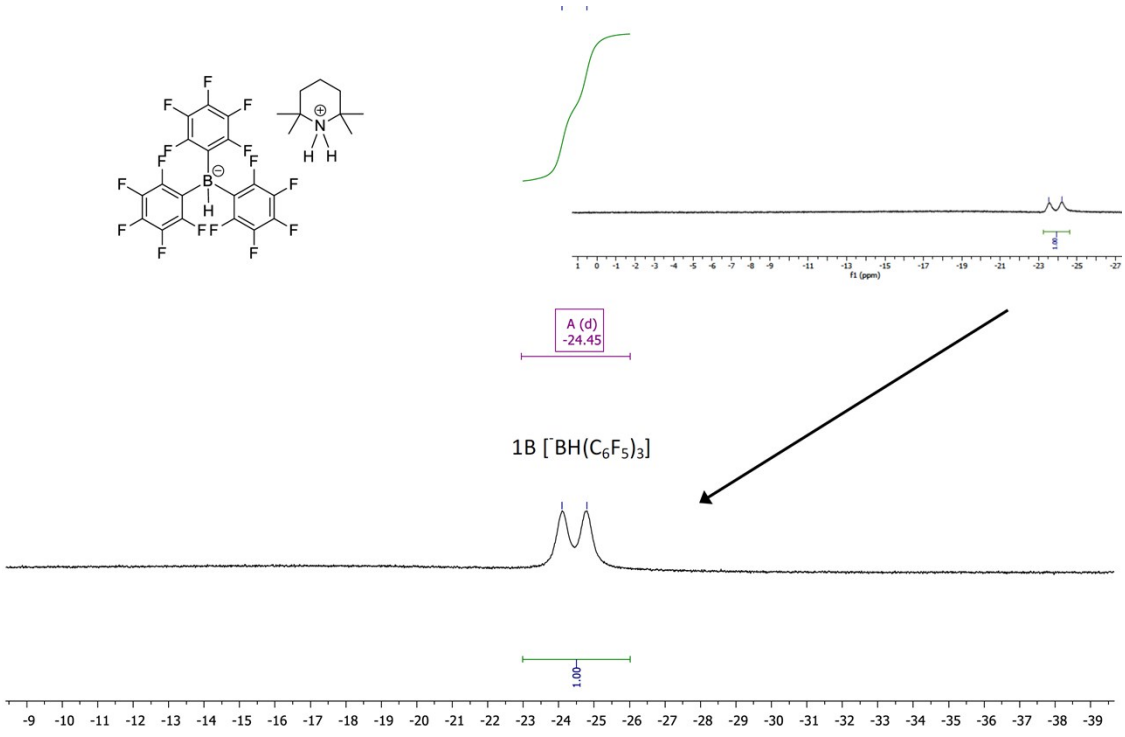

Figure S3. ^{11}B NMR spectrum of [TMPH$^+$][HB(C_6F_5)$_3^-$] (128 MHz, $CDCl_3$)

2.2.- GPC traces

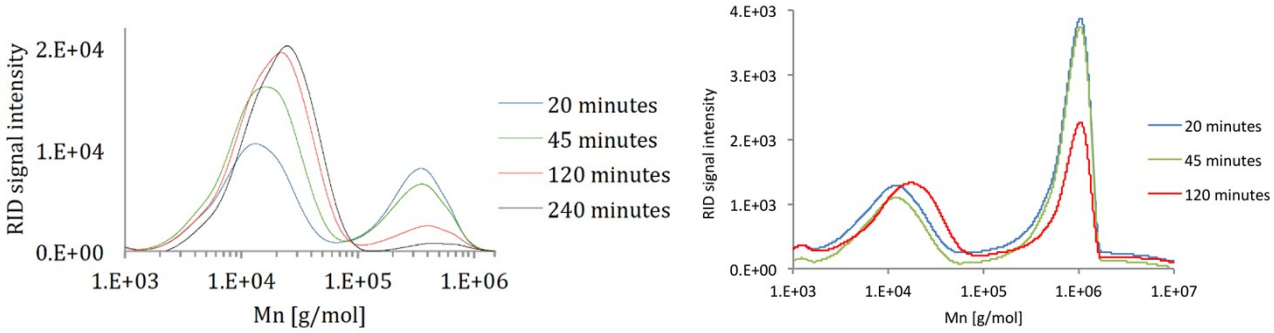

Figure S4. GCP traces of experiments 1 (20 minutes) and 2 (240 minutes) in table 1 (right) and experiment 1 using distilled monomer (left)

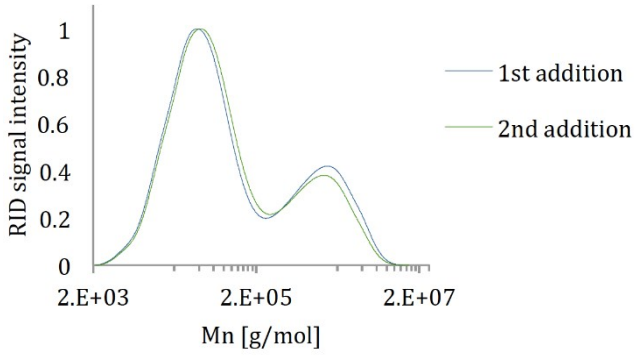

Figure S5. GCP traces of experiment 3 (1st addition) in table 1

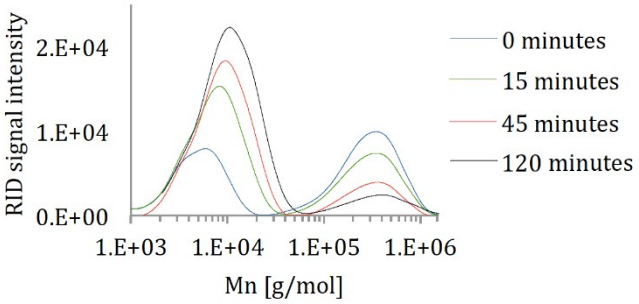

Figure S6. GPC traces of experiment 4 (120 minutes) in table 1

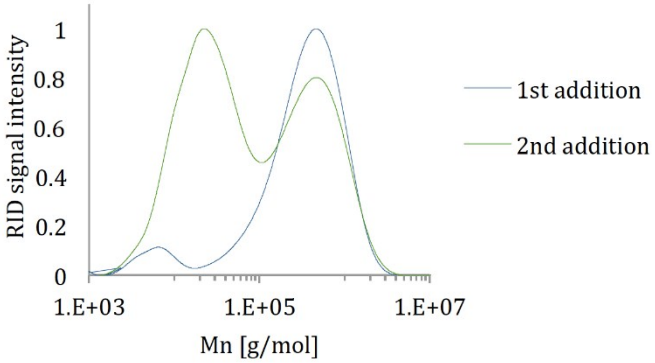

Figure S7. GPC traces of experiment 5 (1st addition) in table 1

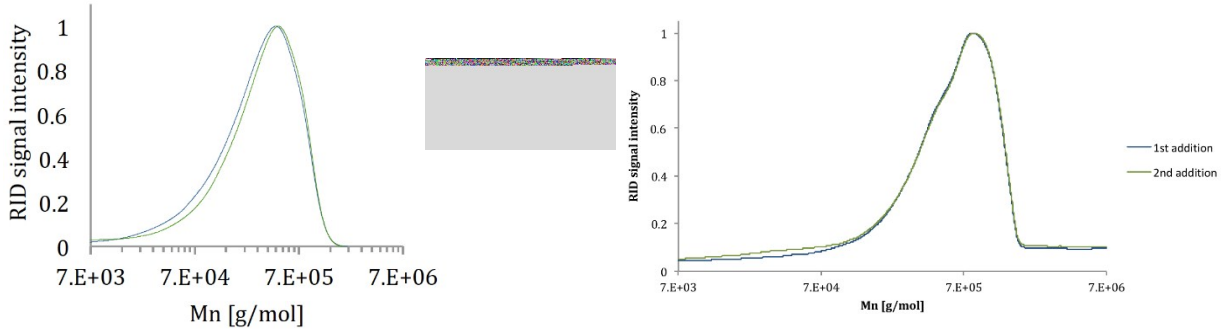

Figure S8. GPC traces of experiment 6 (1st addition) in table 1 (right) and repeated experiment using distilled monomer (left)

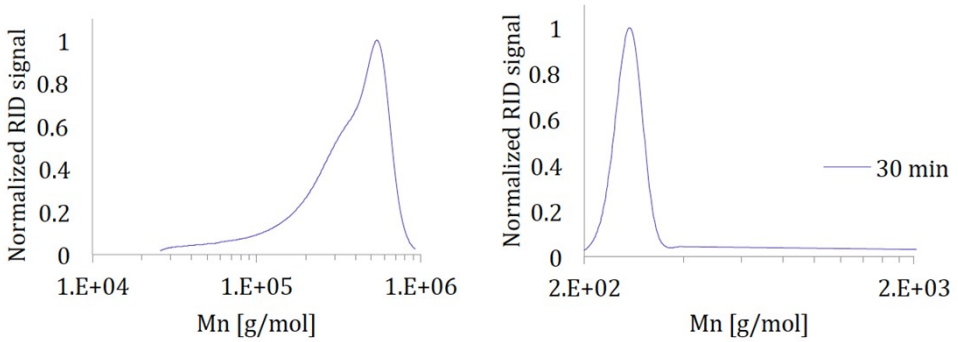

Figure S9. GPC traces of experiments 1 (left) and 2 (right) in table 2

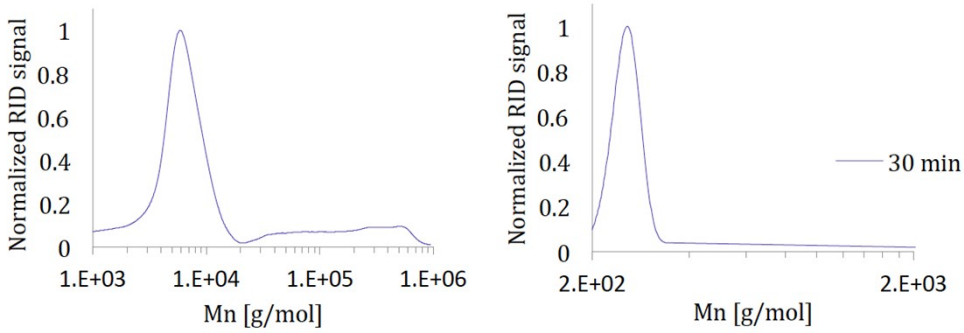

Figure S10. GPC traces of experiments 3 (left) and 4 (right) in table 2

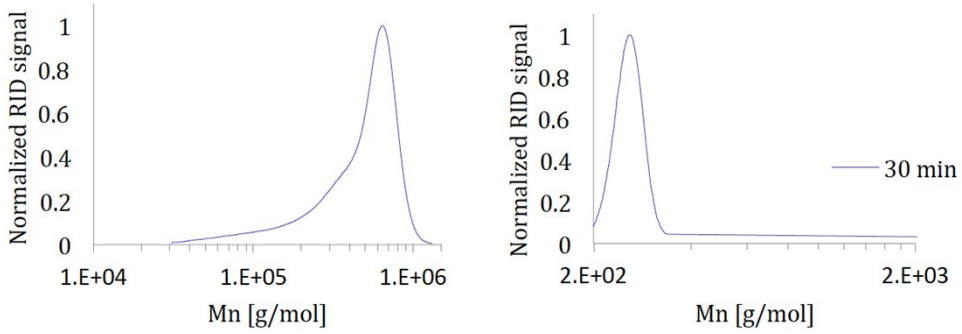

Figure S11. GPC traces of experiments 5 (left) and 6 (right) in table 2

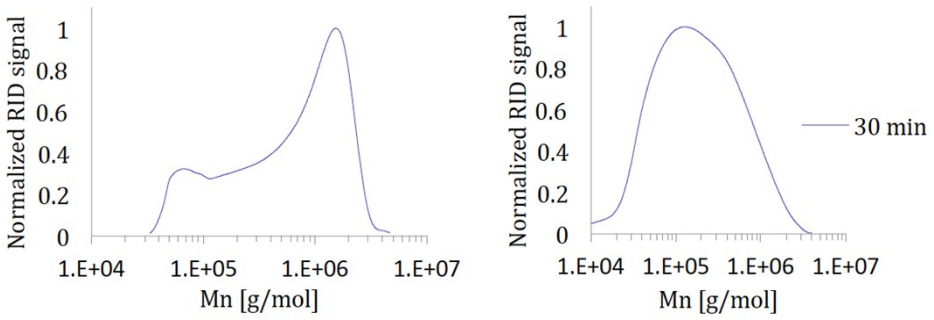

Figure S12. Chromatograms of experiments 7 (left) and 8 (right) in table 2

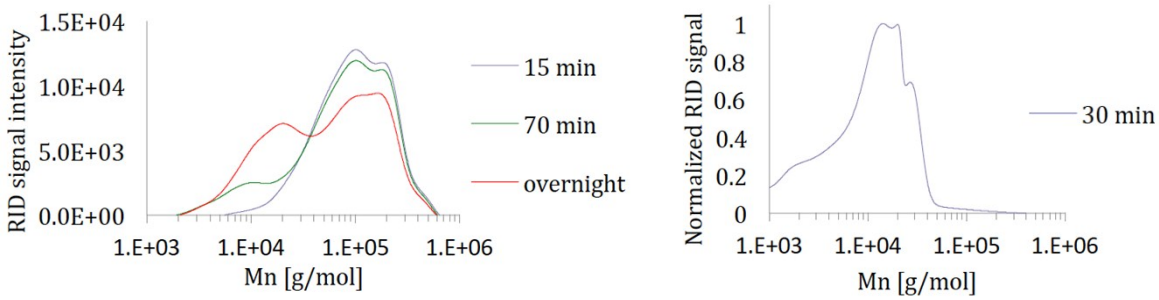

Figure S13. GPC traces of experiments 9 (left, 15 minutes) and 10 (right) in table 2

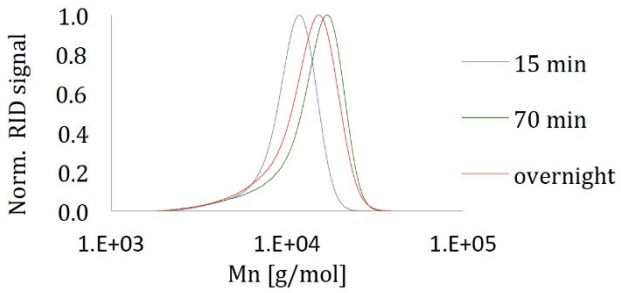

Figure S14. GPC traces of experiment 11 (15 minutes) in table 2

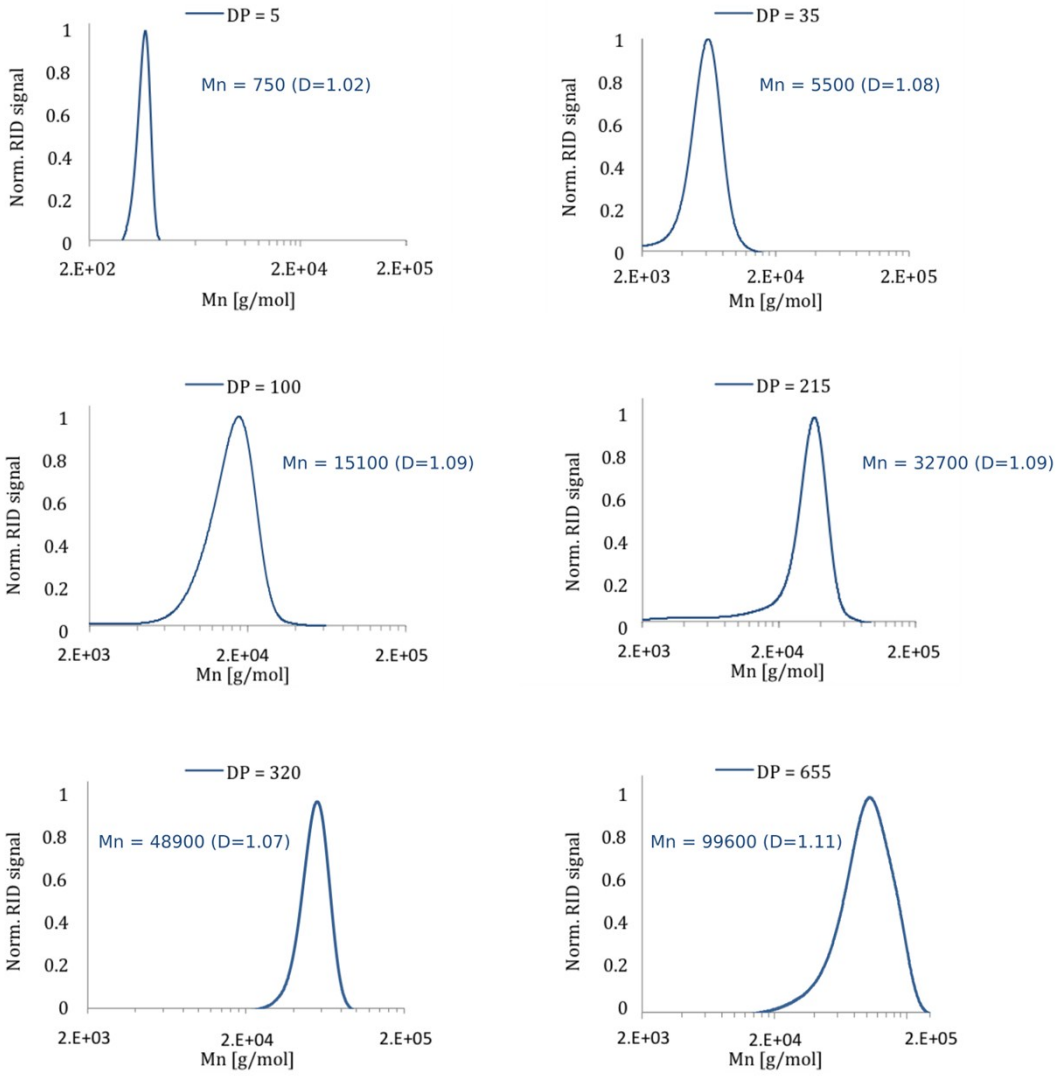

Figure S15. GPC traces of polymerization experiments using different ratio of BCA / $[TMPH^+][HB(C_6F_5)_3^-]$ in THF at 25 ºC to obtain polymers of different degree of polymerization (DP) (See data in Table S1 below)

Table S1. Degree of polymerization and polydispersities of different experiments of the polymerization of BCA, Figure S15, using different ratios of [$TMPH^+$][$HB(C_6F_5)_3^-$] in THF at 25 ºC, following A procedure.

Experiment	DP	Calculated Mn (g/mol)	Experimental Mn (g/mol)[a]	Dispersity (Đ)[a]
S1	5	766	750	1.02
S2	35	5361	5250	1.08
S3	100	15318	15100	1.09
S4	215	32933	32700	1.09
S5	320	49017	48900	1.07
S6	655	100332	98900	1.11

[a]Experimental data obtained by GPC experiments (see Figure S15)

2.3.-GPC Traces, Calorimetric Traces and NMR Spectra for Kinetics / Temperature Dependence Study

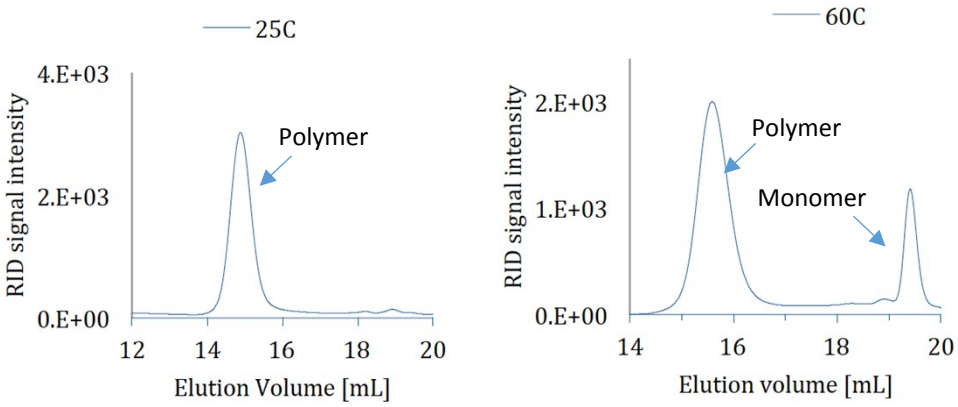

Figure S16. GPC traces at 5 minutes of polymerization time for poly(BCA) initiated by $[TMPH^+][HB(C_6F_5)_3^-]$ in THF at 25 C (left) and 60 C (right)

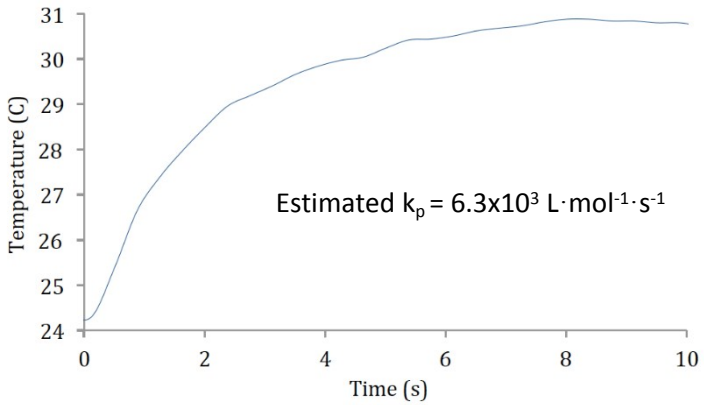

Figure S15. Calorimetric trace of BCA polymerization initiated by PPh_3 in THF at 25 C

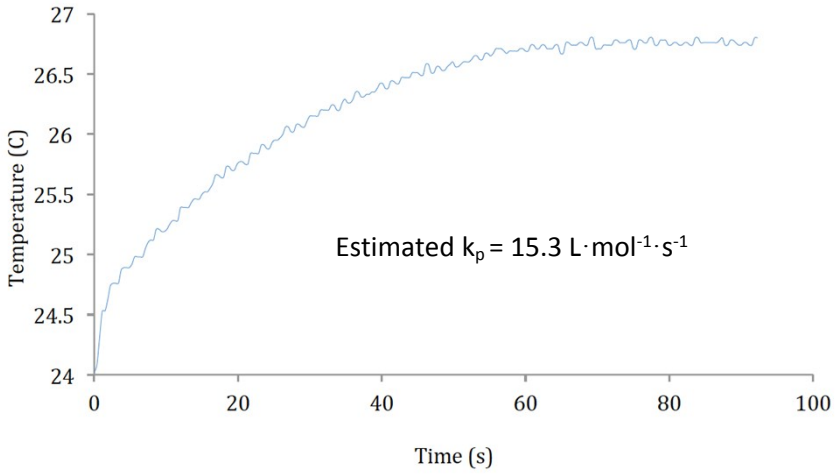

Figure S16. Calorimetric trace of BCA polymerization initiated by $[TMPH^+][HB(C_6F_5)_3^-]$ in THF at 25 C

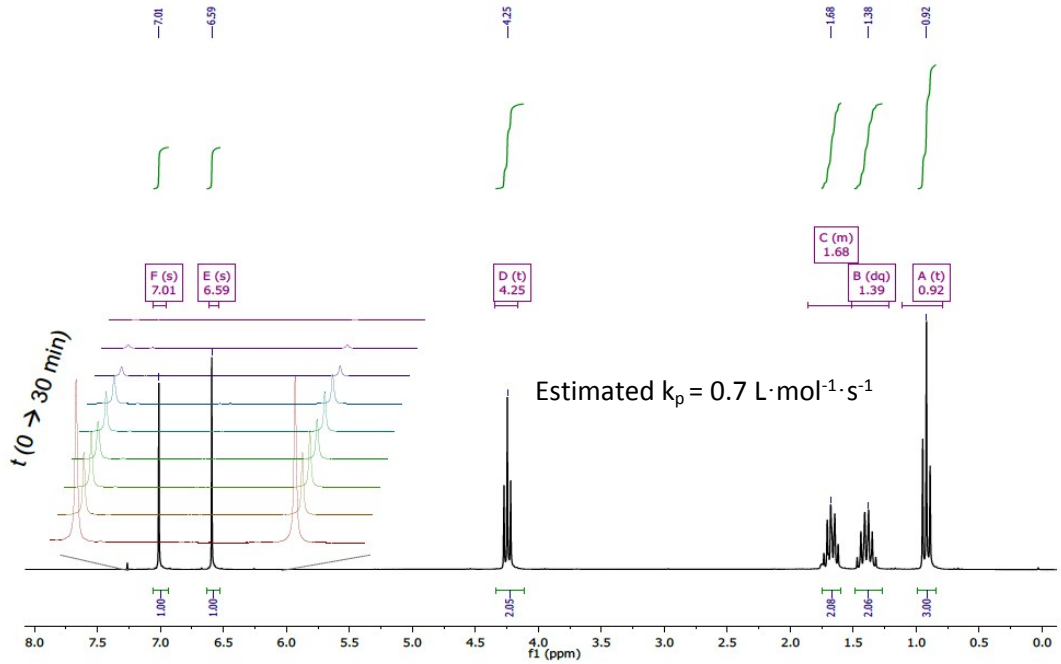

Figure S17. ^{1}H NMR spectrum monitoring BCA / [TMPH$^+$][HB(C_6F_5)$_3^-$] in THF at 60 ºC (250 MHz, $CDCl_3$)

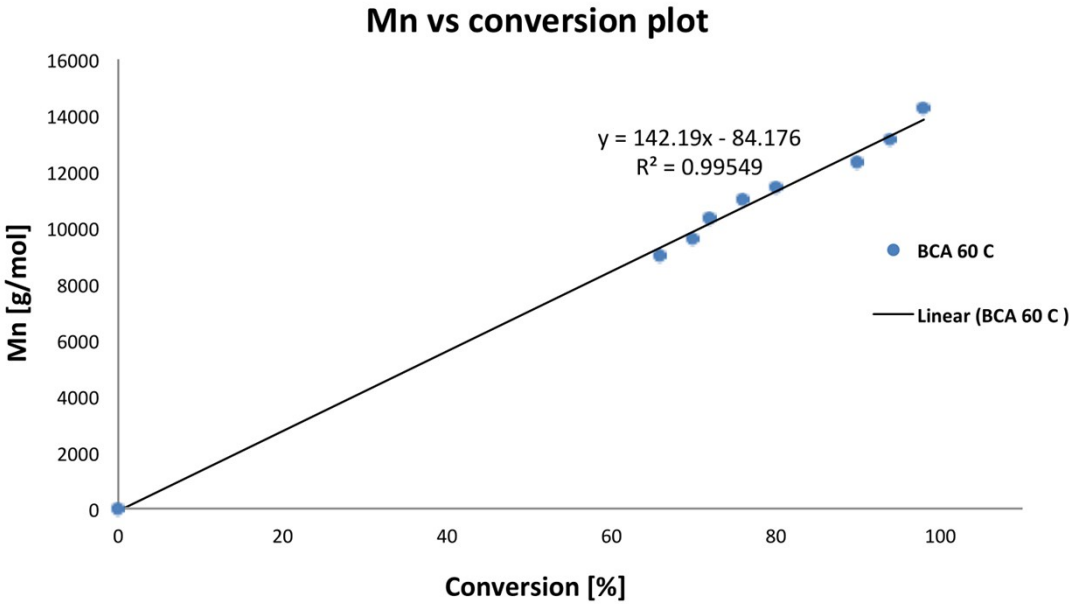

Figure S20. Mn versus Conversion plot of the reaction of BCA / [TMPH$^+$][HB(C_6F_5)$_3^-$] in THF at 60 ºC. Exp. Mn ~ 14400 Da.

Conversions of the reaction were obtained by integration of signals around 7.01 and 6.59 ppm in spectra of ^{1}H NMR compared to signals of ethoxy group at 4.25 (O-C$\underline{H}_2$CH$_3$) and 0.92 ppm (O-CH$_2$C$\underline{H}_3$) in Figure S19, along time. The conversion went up rapidly in the few minutes, showing a linear behaviour when represented against Mn obtained by GPC.

2.4.- NMR Spectra of BCA:[TMPH$^+$][HB(C_6F_5)$_3^-$] / (1:1)

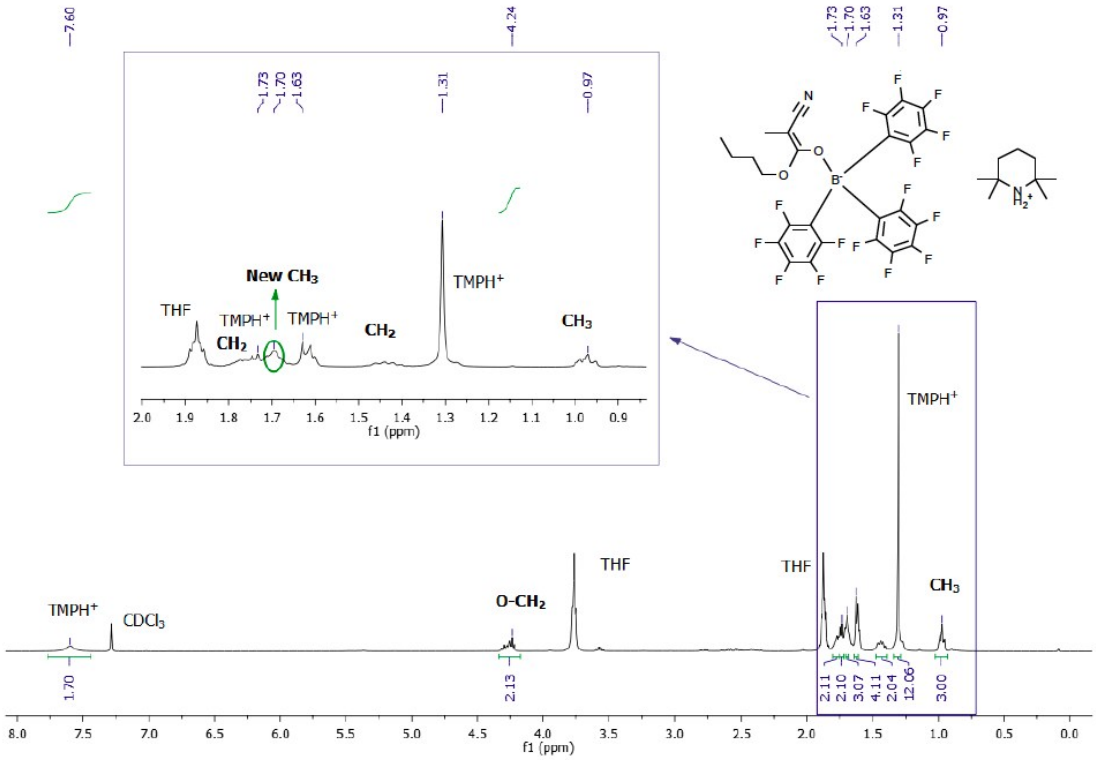

Figure S18. ^{1}H NMR spectrum of BCA:[TMPH$^+$][HB(C_6F_5)$_3^-$] (1:1) isolated solid (250 MHz, $CDCl_3$)

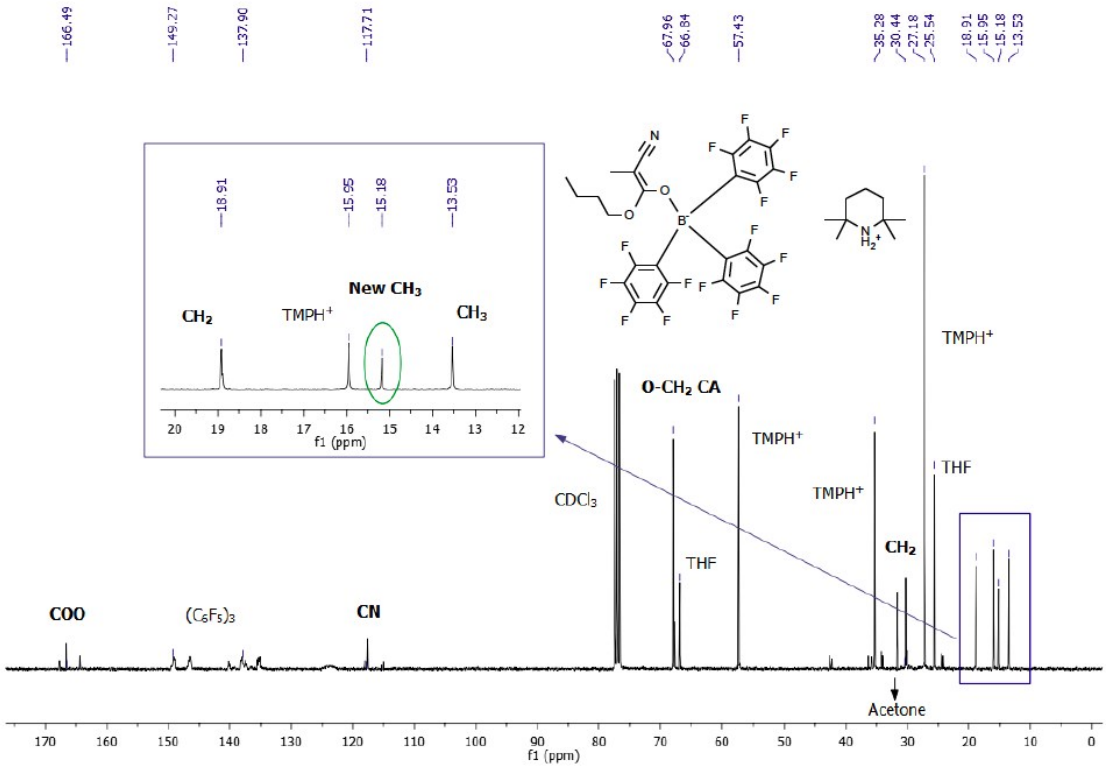

Figure S22. ^{13}C NMR spectrum of BCA:[TMPH$^+$][HB(C_6F_5)$_3^-$] (1:1) isolated solid (100 MHz, $CDCl_3$)

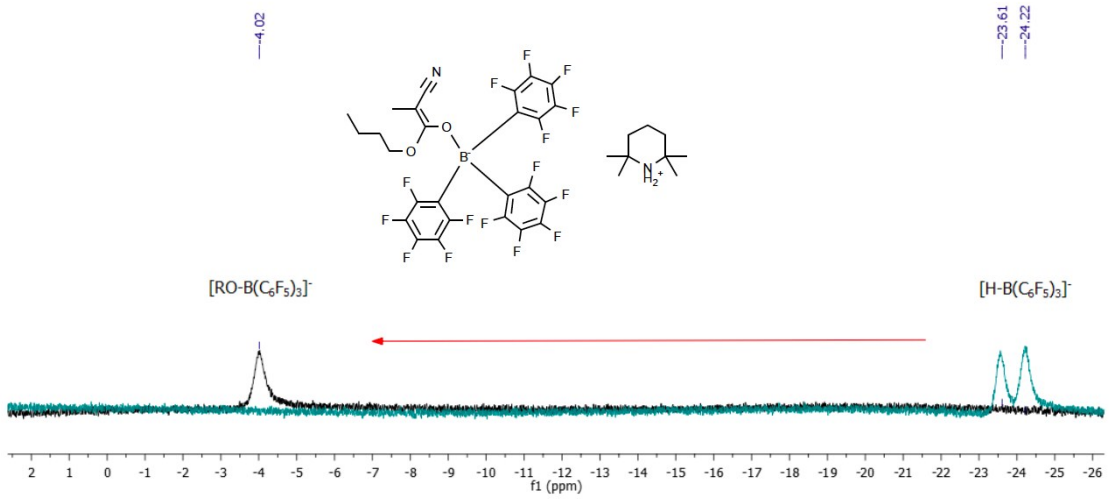

Figure S19. ^{11}B-NMR spectrum of [TMPH$^+$][HB(C_6F_5)$_3^-$] (blue trace) and BCA:[TMPH$^+$][HB(C_6F_5)$_3^-$] (1:1) isolated solid (black trace) (128 MHz, CDCl3)

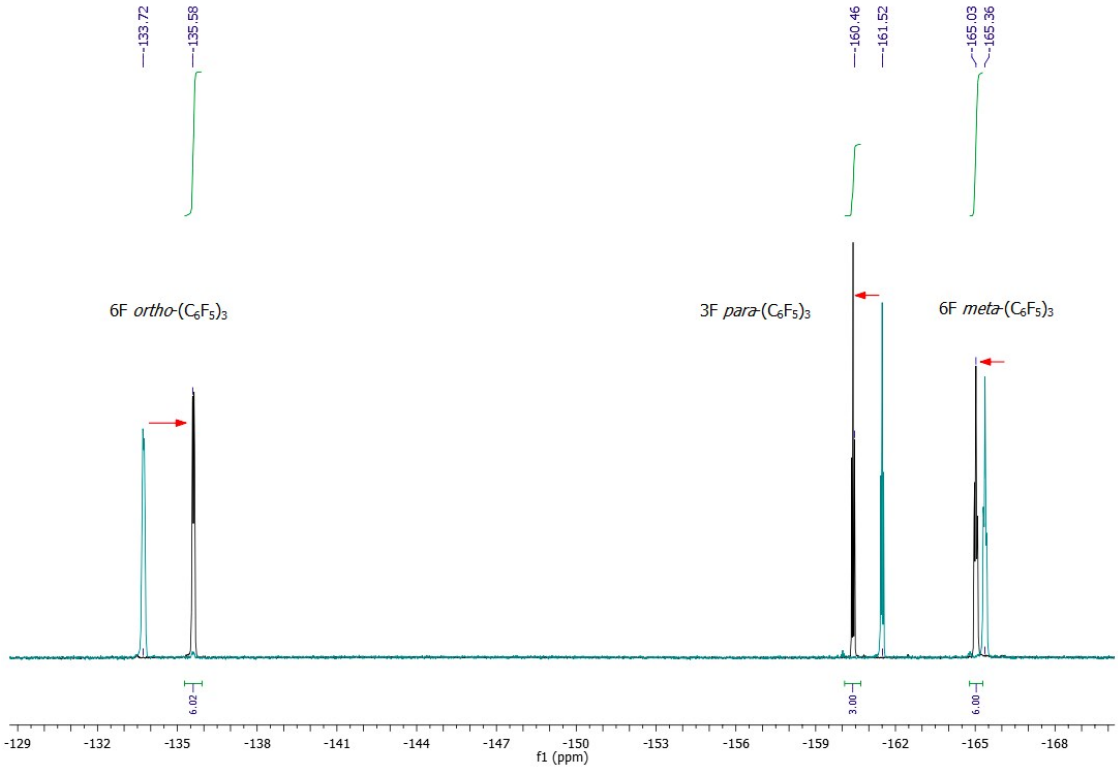

Figure S24. ^{19}F NMR spectrum of [TMPH$^+$][HB(C_6F_5)$_3^-$] (blue trace) and BCA:[TMPH$^+$][HB(C_6F_5)$_3^-$] (1:1) isolated solid (black trace) (235 MHz, CDCl3)

2.5.- NMR Spectra of Poly(cyanoacrylates)

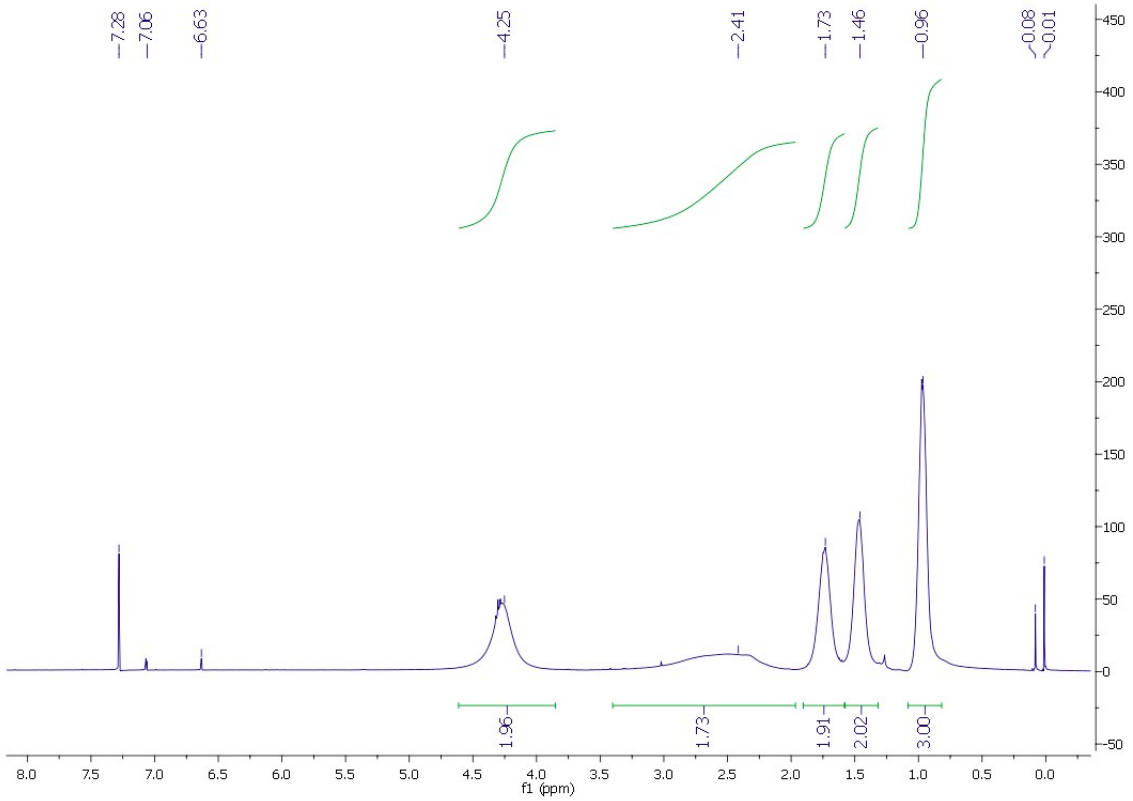

Figure S25. ^{1}H NMR spectrum of poly(BCA) initiated by [TMPH^{+}][HB(C_6F_5)$_3^{-}$] (250 MHz, $CDCl_3$)

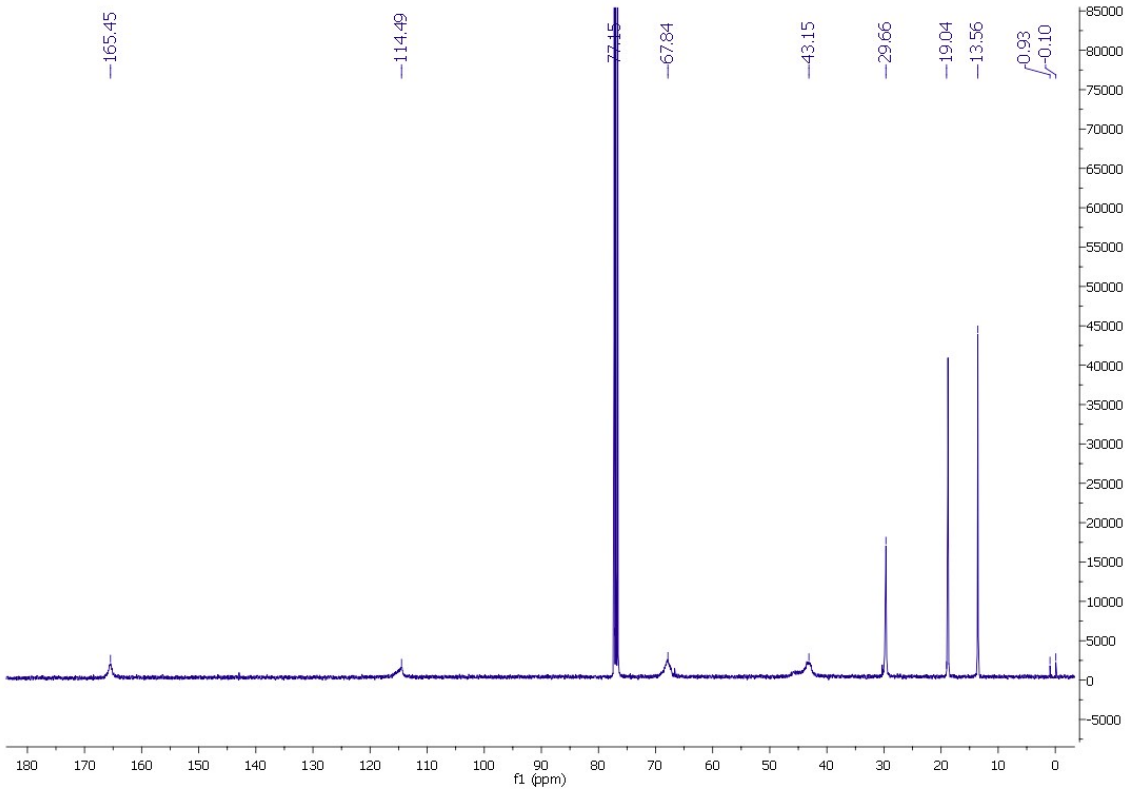

Figure S20. ^{13}C NMR spectrum of poly(BCA) initiated by [TMPH^{+}][HB(C_6F_5)$_3^{-}$] (100 MHz, $CDCl_3$)

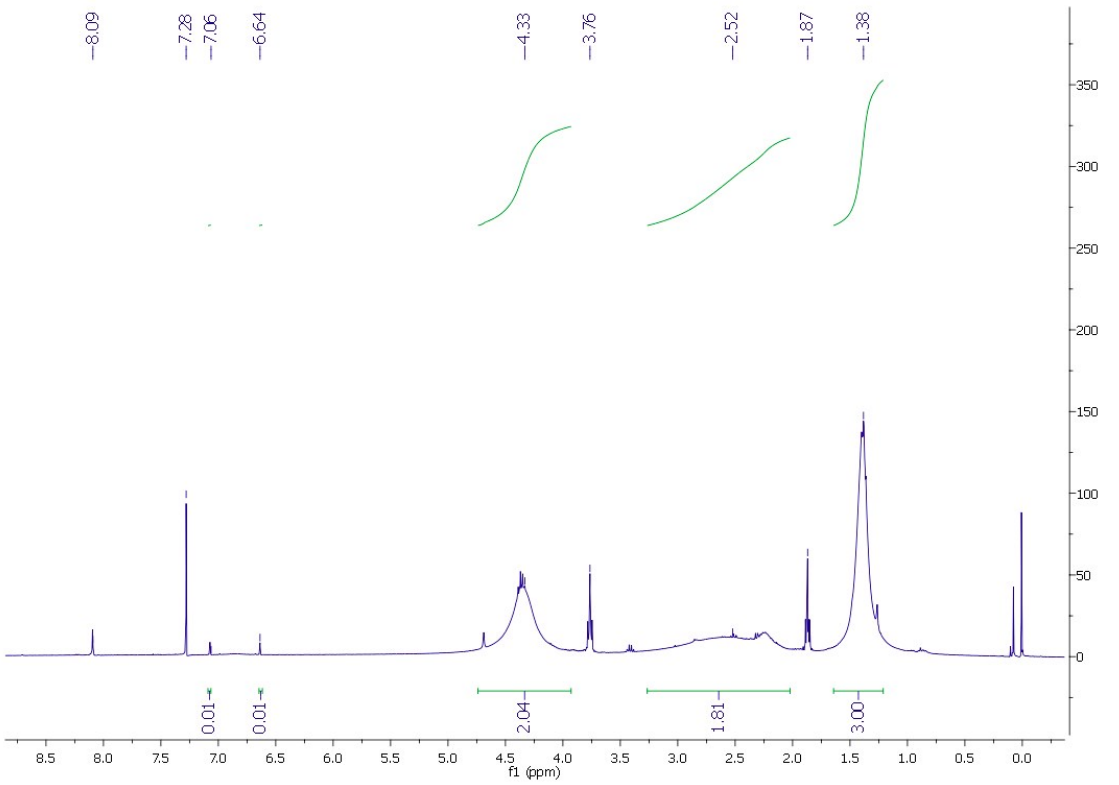

Figure S21. ^{1}**H NMR spectrum of poly(ECA) initiated by [TMPH^{+}][HB(C$_6$F$_5$)$_3^{-}$] (250 MHz, CDCl$_3$)**

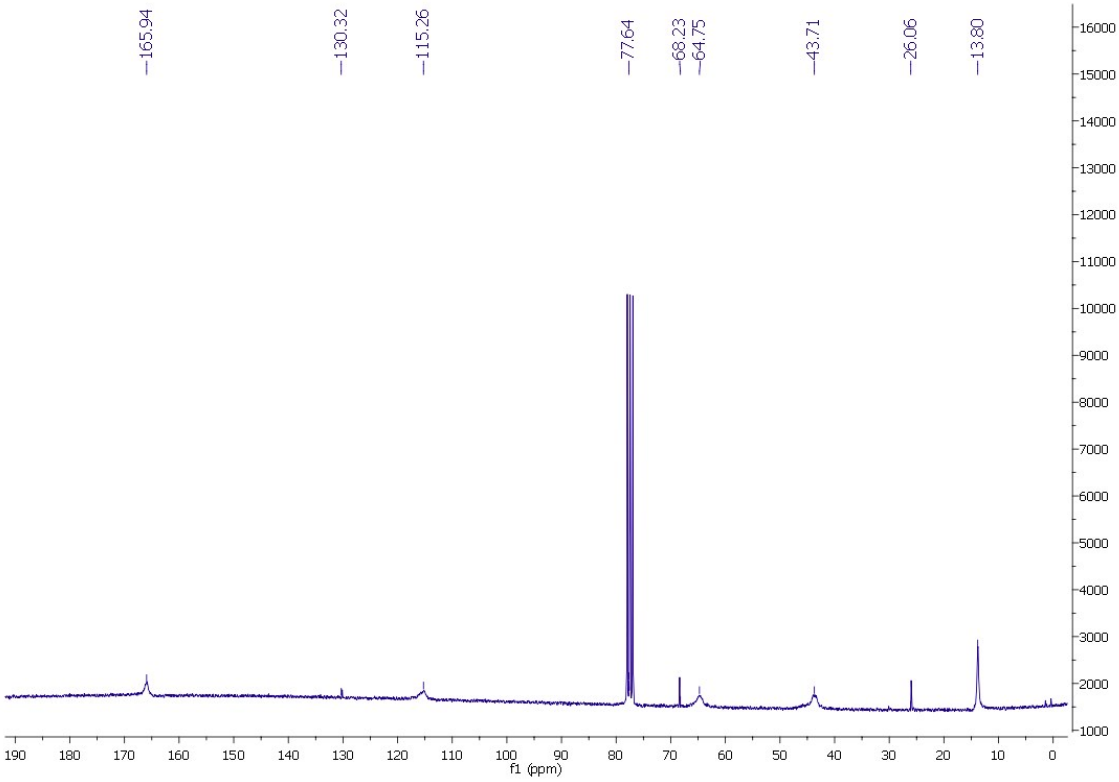

Figure S28. ^{13}**C NMR spectrum of poly(ECA) initiated by [TMPH^{+}][HB(C$_6$F$_5$)$_3^{-}$] (100 MHz, CDCl$_3$)**

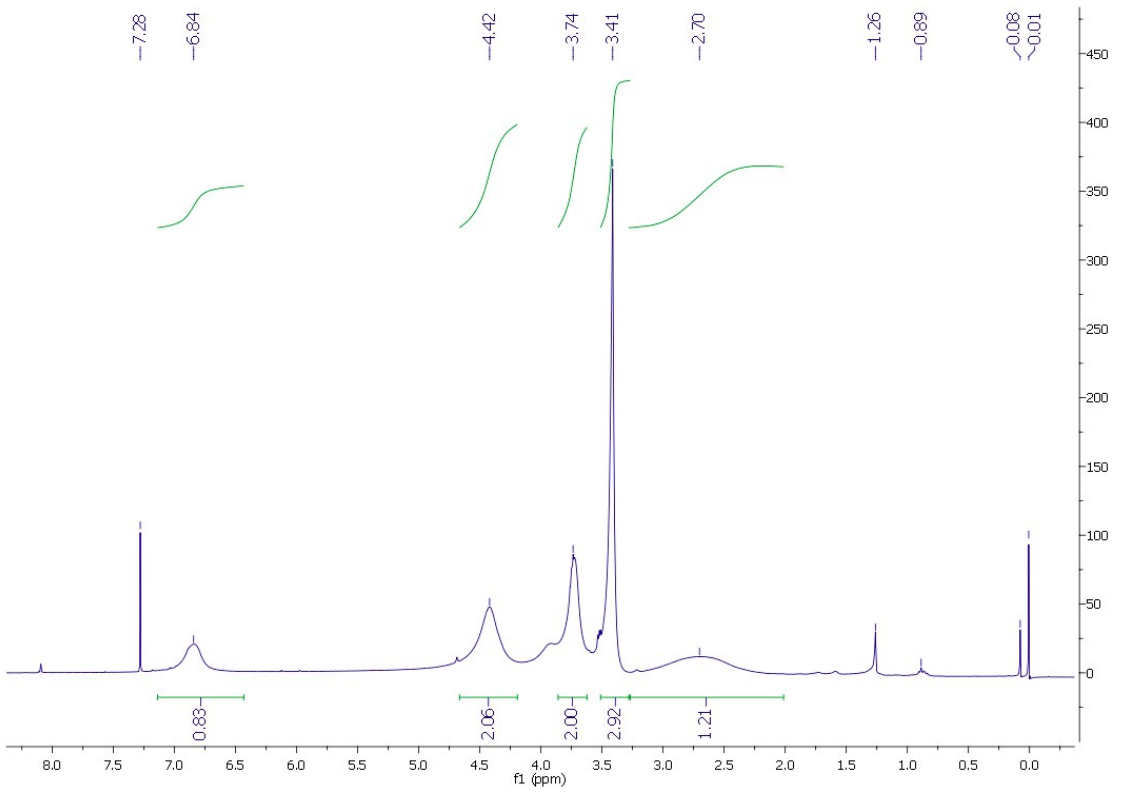

Figure S22. ^{1}H NMR spectrum of poly(MECA) initiated by [TMPH^{+}][HB(C_6F_5)$_3^{-}$] (100 MHz, $CDCl_3$)

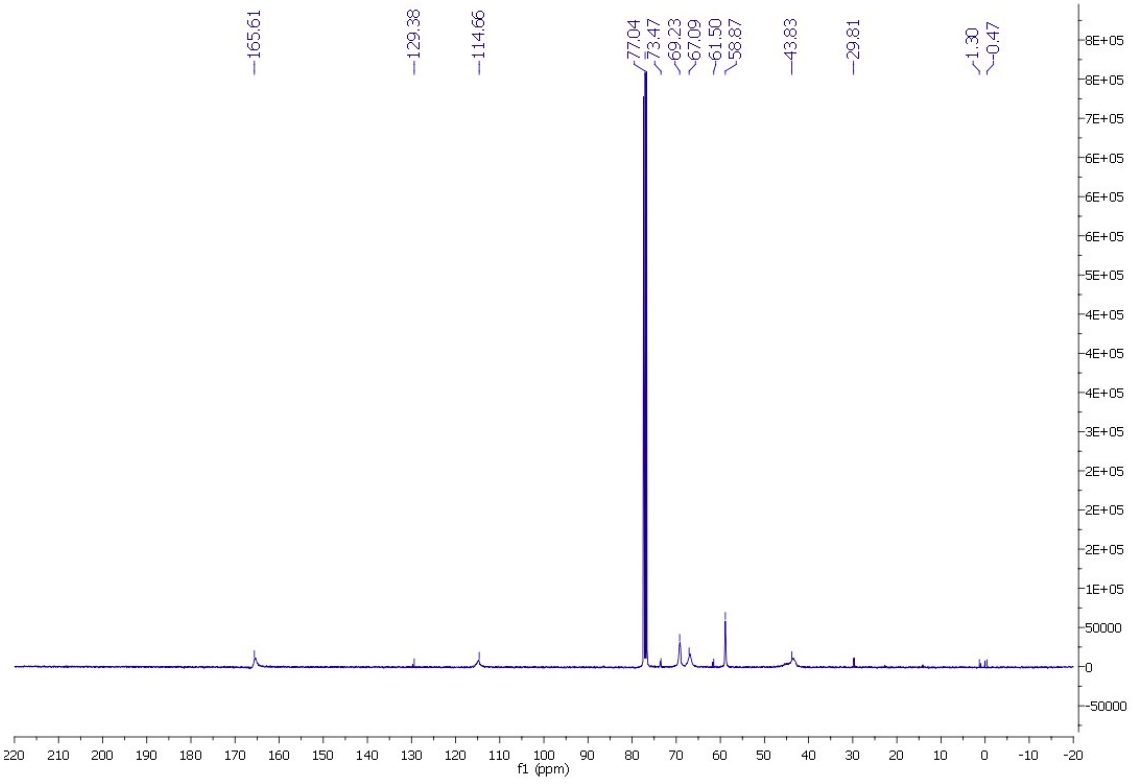

Figure S30. ^{13}C NMR spectrum of poly(MECA) initiated by [TMPH^{+}][HB(C_6F_5)$_3^{-}$] (100 MHz, $CDCl_3$)

2.6.-MALDI-TOF MS Chromatograms of Poly(cyanoacrylates)

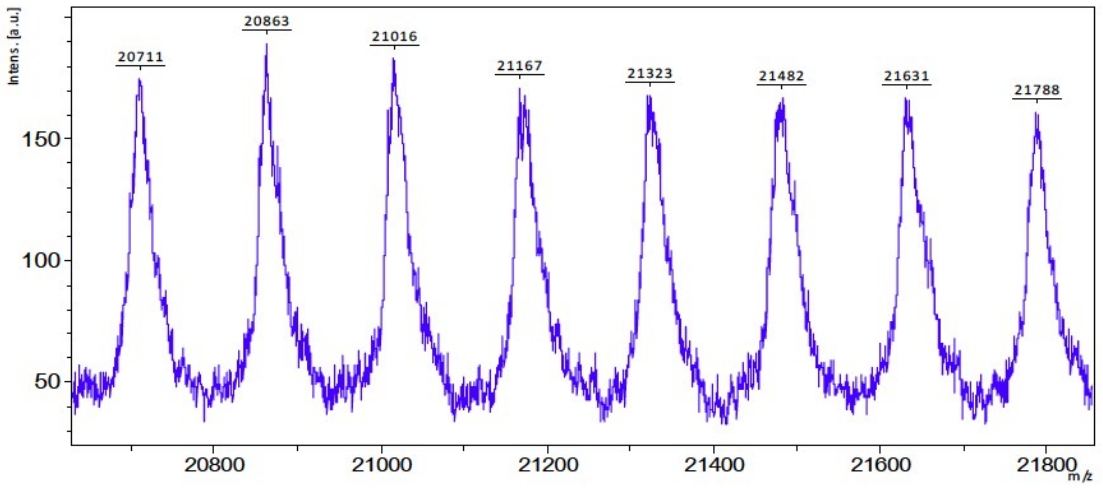

Figure S31. MALDI-TOF MS chromatograms of poly(BCA) initiated by $[TMPH^+][HB(C_6F_5)_3^-]$

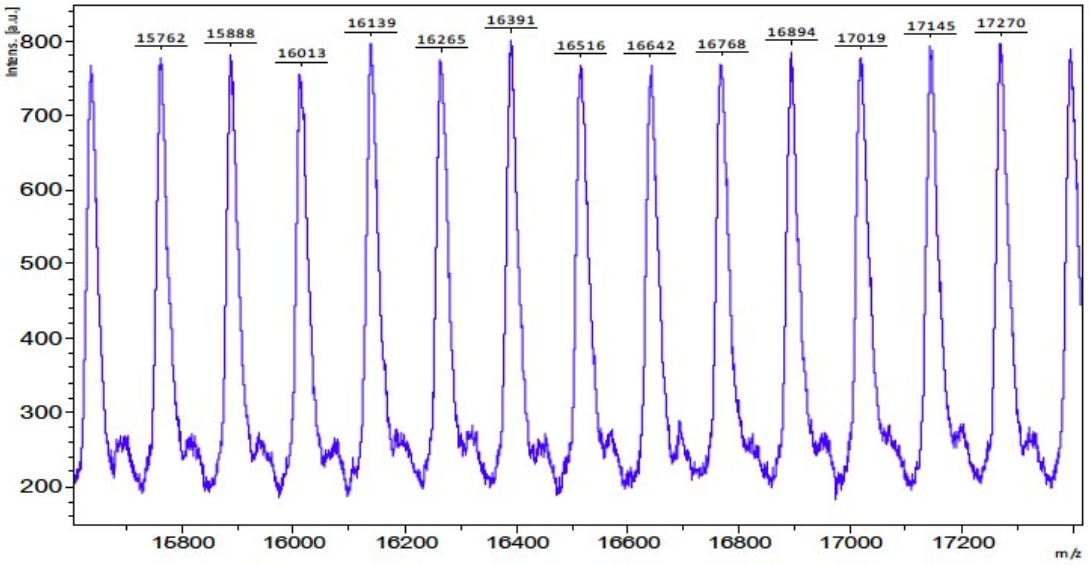

Figure S32. MALDI-TOF MS chromatograms of poly(ECA) initiated by $[TMPH^+][HB(C_6F_5)_3$

3. *References*

[1] V. Sumerin, F. Schulz, M. Nieger, M. Leskelä, T. Repo, B. Rieger, *Angew. Chem. Int. Ed.* **2008**, *47*, 6001-6003.