

Precision design of ethylene- and polar-monomer-based copolymers by  
organometallic-mediated radical polymerization

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## 1- Materials.

All manipulations were performed by classical Schlenk techniques under argon. Vinyl acetate (VAc, >99 %, Aldrich), Acrylonitrile (AN, 99%, Aldrich) and *N*-methyl-*N*-vinyl acetamide (NMVA, 98 %, Aldrich) were dried over calcium hydride, degassed by several freeze-thawing cycles before distillation under reduced pressure and stored under argon. Dimethyl sulfoxide DMSO, hexane and *tert*-Butylbenzene were purchased from Aldrich, dried using 4 Å molecular sieves and degassed under argon. Ethylene (N35, 99.95%) was purchased from Air Liquide and used as received. *Bis*-(acetylacetonato)cobalt(II) (Co(acac)<sub>2</sub>) (>98%, Acros) was stored under argon and used as received. 2,2,6,6-tetramethylpiperidine 1-oxy (TEMPO, 98%, Aldrich), CHCl<sub>3</sub> (99+%, Acros) and 1-bromooctane (99%, Aldrich) were used as received. 2,2'-azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70, 96%, Wako) and *N-tert*-Butyl- $\alpha$ -phenylnitron (PBN, 98%, Aldrich) were stored at -20°C and used as received. The organo-cobalt(III) adduct initiator [Co(acac)<sub>2</sub>-(CH(OCOCH<sub>3</sub>)CH<sub>2</sub>)<sub>4</sub>-R<sub>0</sub>], where R<sub>0</sub> being the primary radical generated by 2,2'-azo-bis(4-methoxy-2,4-dimethyl valeronitrile) (V-70, Wako), was prepared as described previously<sup>1</sup> and stored as a CH<sub>2</sub>Cl<sub>2</sub> solution at -20°C under argon.

## 2- Characterizations.

The molar masses ( $M_n$ ) and molar mass distributions ( $M_w/M_n$ ) of the EVA copolymers were determined by size-exclusion chromatography (SEC) in tetrahydrofuran (THF) relative to poly(styrene) (PS) standards at 45 °C (flow rate: 1 mL/min) with a SFD-S5200 autosampler liquid chromatograph equipped with a SFD-2000 refractometer index detector as well as Styragel HR columns (four HP PL gel 5  $\mu$ m columns: 10<sup>5</sup>, 10<sup>4</sup>, 10<sup>3</sup> and 10<sup>2</sup> Å or three HP PL gel 5  $\mu$ m columns: 10<sup>4</sup>, 10<sup>3</sup> and 10<sup>2</sup> Å).

The molar masses ( $M_n$ ) and molar mass distributions ( $M_w/M_n$ ) of the AN-ethylene and NMVA-ethylene copolymers were determined by size-exclusion chromatography (SEC) in dimethylformamide (DMF) containing LiBr (0.025 M) at 55 °C (flow rate: 1 mL/min) with a Waters 600 liquid chromatograph equipped two PSS GRAM analytical columns (1000 Å, 8\*300 mm, particle size 10 µm) and one PSS GRAM analytical column (30 Å, 8\*300 mm, particle size 10 µm). The absolute molar masses of the copolymer were determined by SEC equipped with a multiangle laser light scattering (MALLS) detector in DMF/LiBr (0.025 M). The Wyatt MALLS detector (120 mW solid-state laser,  $k = 1/4$  658 nm, DawnHeleos S/N342-H) measures the excess Rayleigh ratio  $R_h$  (related to the scattered intensity) at different angles for each slice of the chromatogram. The specific refractive index increment ( $dn/dc$ ) of each (co)polymer was measured by using a Wyatt Optilab refractive index detector ( $\lambda = 658$  nm). Data were processed with the Astra V software (Wyatt Technology).

Elemental analyses were performed at Service de Microanalyse, ICSN-CNRS, 91198 Gif-sur-Yvette, France. Oxygen titration was performed using an Elementar Vario micro Cube analyzer equipped with a catharometer.

Differential scanning calorimetry (DSC) measurements were acquired with a TA Instruments Q1000 DSC, using standard aluminum pans, an indium standard for calibration, and nitrogen as the purge gas. Glass transition temperatures of copolymers were measured by the inflection points in the heating thermograms.

$^1\text{H}$  NMR spectra of reaction mixtures for the determination of the conversions were recorded in  $\text{CDCl}_3$  (EVA or E/NMVA copolymers) or  $\text{DMSO-D}_6$  (E/AN copolymer) at 298K with a 250 MHz Bruker spectrometer. After purification  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR (DEPTQ) and heteronuclear single quantum coherence spectroscopy (HSQC) spectra of final polymers were recorded with a 500 MHz Bruker spectrometer.

ESR studies were carried out with a Miniscope MS400 (Magnetech, Berlin, Germany) benchtop spectrometer working at X-band with a modulation amplitude of 200 G, a sweep width of 68 G, a sweep time of 30 s, and a microwave power of 10 mW. The temperature was adjusted at 25 °C using a temperature controlled unit TC H03 (Magnetech). All manipulations were performed under argon using a schlenk-type analytical tube (volume: 0.12 mL). The ESR spectra simulations were carried out with the PEST WINSIM program.<sup>2</sup>

### 3- Copolymerization procedures

#### 3.1. Copolymerization of VAc and ethylene

Copolymerization of VAc and ethylene is described in the main article. Results are summarized in Table 1, entry 1. Complete kinetics of polymerization are summarized in Figure 1 and Supplementary, Fig. 1 (for polymerizations at 10, 25 and 50 bar) and Supplementary, Fig. 2 (for polymerizations at 25 bar with VAc/Co ratio of 100 or 400). Elemental analysis (EVA<sub>10 bar</sub>: C, 57.4%, O, 35.2%; EVA<sub>50 bar</sub>: C, 62.8%, O, 27.7%). NMR characterizations of EVA copolymers are detailed below. The amount of ethylene was evaluated by integration of signals of the 0.9-2.2 ppm region (assigned to CH<sub>2</sub> repeating units of ethylene and to CH<sub>2</sub> and CH<sub>3</sub> repeating units of VAc, Figure 3) then subtracting 5 × integral of CH of VAc (centered at 5 ppm, Figure 3). Compositions and molecular parameters of EVAs are presented in Table 1, entry 1.

#### 3.2. Copolymerization of ethylene and NMVA

A solution of organo-cobalt(III) initiator [Co(acac)<sub>2</sub>-(CH(OCOCH<sub>3</sub>)CH<sub>2</sub>)<sub><4</sub>-R<sub>0</sub>)] in CH<sub>2</sub>Cl<sub>2</sub> (4.0 mL of a 0.10 M stock solution, 2.2 10<sup>-4</sup> mol) was introduced under argon in a 30 mL Schlenk tube and evaporated to dryness under reduced pressure at room temperature. A volume of NMVA (2.2 mL, 0.021 mol) was added under argon and the solution was then transferred into a 30 mL stainless steel TopIndustrie autoclave under an ethylene atmosphere using a cannula. The autoclave was pressurized under the desired ethylene pressure (10 or 50 bar) and heated at 40 °C using an oil bath. The pressure (10 or 50 bar) was manually maintained during the polymerization and the reaction mixture was magnetically stirred at 500 rpm. After 24 h of reaction, ethylene was removed and an aliquot was picked out the reaction medium to evaluate the VAc conversion by <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub>. A degassed solution of TEMPO (120 mg, 7.7 10<sup>-4</sup> mol) in DMF (5 mL) was introduced in the reactor under argon and let to react for 1 h at 60 °C in order to eliminate the cobalt complex from the copolymer chain-end, according to a previous report.<sup>3</sup> The polymer was recovered by precipitation in diethyl ether (100 mL), filtered, dried under reduced pressure and purified by overnight dialysis in deionized water using a Spectra/Por\_7 dialysis membrane (1 kD). The molecular parameters of the copolymer were measured by SEC in DMF using a MALLS detector (EMMVA<sub>10 bar</sub>: dn/dc = 0.0836 mL/g, M<sub>n</sub> = 9100 g/mol; EMMVA<sub>50 bar</sub>: dn/dc = 0.0818 mL/g, M<sub>n</sub> = 4700 g/mol) and the composition of the copolymer was determined by <sup>1</sup>H NMR in CDCl<sub>3</sub> and elemental analysis (E/NMVA<sub>10 bar</sub>: C, 60.5%, N, 14.1%; E/NMVA<sub>50 bar</sub>: C, 60.9% N, 11.0%). Compositions and molecular parameters of ENMVAs are presented in

Table 1, entry 2. A typical  $^1\text{H}$  NMR spectrum of E/MMVA copolymer is shown in Supplementary, Fig. 6. The amount of ethylene was evaluated by integration of signals of the 0.9-1.7 ppm region (assigned to  $\text{CH}_2$  repeating units of ethylene and to  $\text{CH}_2$  repeating units of MMVA, Supplementary, Fig. 6) then subtracting integral of  $\text{NCH}_3$  of MMVA (centered at 2.75 ppm, Supplementary, Fig. 6).

### 3.3. Copolymerization of ethylene and AN

A solution of organo-cobalt(III) initiator  $[\text{Co}(\text{acac})_2-(\text{CH}(\text{OCOCH}_3)\text{CH}_2)_{<4}\text{-R}_0]$  in  $\text{CH}_2\text{Cl}_2$  (8.0 mL of a stock solution,  $4.5 \times 10^{-4}$  mol) was introduced under argon in a 30 mL Schlenk tube and evaporated to dryness under reduced pressure at room temperature. A volume of DMSO (5 mL) and AN (3.0 mL, 0.046 mol) were added under argon at  $0^\circ\text{C}$  and the solution was then transferred into a 30 mL stainless steel TopIndustrie autoclave under an ethylene atmosphere using a cannula. The autoclave was pressurized under the desired ethylene pressure (10 or 50 bar) and heated at  $40^\circ\text{C}$  using an oil bath. The pressure (10 or 50 bar) was manually maintained during the polymerization and the reaction mixture was magnetically stirred using a stirring bar at 500 rpm. After 24 h of reaction, ethylene was removed and an aliquot was carried out to determine the VAc conversion by  $^1\text{H}$  NMR spectroscopy in  $\text{DMSO-}D_6$ . A degassed solution of TEMPO (120 mg,  $7.7 \times 10^{-4}$  mol) in DMF (5 mL) was introduced in the reactor under argon and let to react for 1 h at  $60^\circ\text{C}$  in order to eliminate the cobalt complex from the copolymer chain-end, according to a previous report.<sup>3</sup> The polymer was recovered by precipitation in diethyl ether (200 mL), filtered and dried under reduced pressure at  $75^\circ\text{C}$ . The molecular parameters of the copolymer were measured by SEC in DMF using a MALLS detector ( $\text{EAN}_{10 \text{ bar}}$ :  $\text{dn/dc} = 0.0780 \text{ mL/g}$ ,  $M_n = 23700 \text{ g/mol}$ ;  $\text{EAN}_{50 \text{ bar}}$ :  $\text{dn/dc} = 0.0776 \text{ mL/g}$ ,  $M_n = 24900 \text{ g/mol}$ ) and the composition of the copolymer was determined by  $^1\text{H}$  NMR in  $D_6$ -DMSO and elemental analysis ( $\text{E/AN}_{10 \text{ bar}}$ : C, 65.3%, H, 6.1%, N, 27.2%;  $\text{E/AN}_{50 \text{ bar}}$ : C, 65.9%, H, 5.9%, N, 25.4%). Compositions and molecular parameters of EAN are presented in Table 1, entry 3.

The  $^1\text{H}$  NMR spectrum, DEPTQ spectrum and HSQC of  $\text{E/AN}_{50 \text{ bar}}$  are shown in Supplementary, Fig.7-9, respectively. The amount of ethylene was evaluated by integration of signals of the 1.5-1.8 ppm region (assigned to  $\text{CH}_2$  repeating units of ethylene Supplementary, Fig. 7).

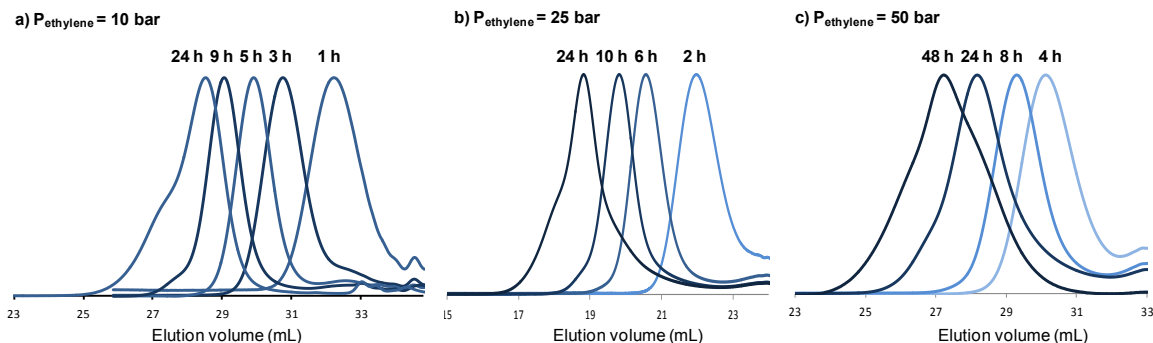
### 3.4. Ethylene/VAc diblock copolymer synthesis (( $\text{EVA}_{50 \text{ bar}}$ )-*b*-( $\text{EVA}_{10 \text{ bar}}$ )).

A solution of organo-cobalt(III) initiator  $[\text{Co}(\text{acac})_2-(\text{CH}(\text{OCOCH}_3)\text{CH}_2)_{<4}\text{-R}_0]$  in  $\text{CH}_2\text{Cl}_2$  (4.0 mL of a 0.10 M stock solution,  $4 \times 10^{-4}$  mol) was introduced under argon in a 30 mL

Schlenk tube and evaporated to dryness under reduced pressure at room temperature. A volume of VAc (3.7 mL,  $4 \times 10^{-2}$  mol) was added under argon and the solution was then transferred into a 30 mL stainless steel TopIndustrie autoclave under an ethylene atmosphere using a cannula. The autoclave was pressurized at 50 bar by ethylene and heated at 40 °C using an oil bath. The pressure was manually maintained during the polymerization and the reaction mixture was magnetically stirred at 500 rpm. After 10 h of reaction, the autoclave was depressurized (a low ethylene flux was maintained) and an aliquot was picked out the medium to determine the VAc conversion and the copolymer composition (after removing of VAc under reduced pressure) by  $^1\text{H}$  NMR spectroscopy in  $\text{CDCl}_3$  and the molecular parameters of the copolymer by SEC in THF after TEMPO treatment.<sup>4</sup> After sampling, the autoclave was pressurized to 10 bar. After 14 h of reaction, the autoclave was depressurized and an aliquot was picked out the medium under argon to evaluate the VAc conversion by  $^1\text{H}$  NMR spectroscopy in  $\text{CDCl}_3$ . At the end of the experiment a degassed solution of TEMPO (120 mg,  $7.7 \times 10^{-4}$  mol) in THF (5 mL) was introduced in the reactor under argon and let to react for 1 h at 60 °C in order to eliminate the cobalt complex from the copolymer chain-end, according to a previous report.<sup>3</sup> The polymer was recovered by precipitation in heptane (100 mL), filtered and dried under reduced pressure at 75 °C. The molecular parameters of the copolymer were measured by SEC in THF using PS as a calibration and the composition of the copolymer was determined by  $^1\text{H}$  NMR in  $\text{CDCl}_3$ .

Results are summarized in Table 3 and Figure 4 for (EVA<sub>50 bar</sub>)-*b*-(EVA<sub>10 bar</sub>).

## 4- Supplementary figures

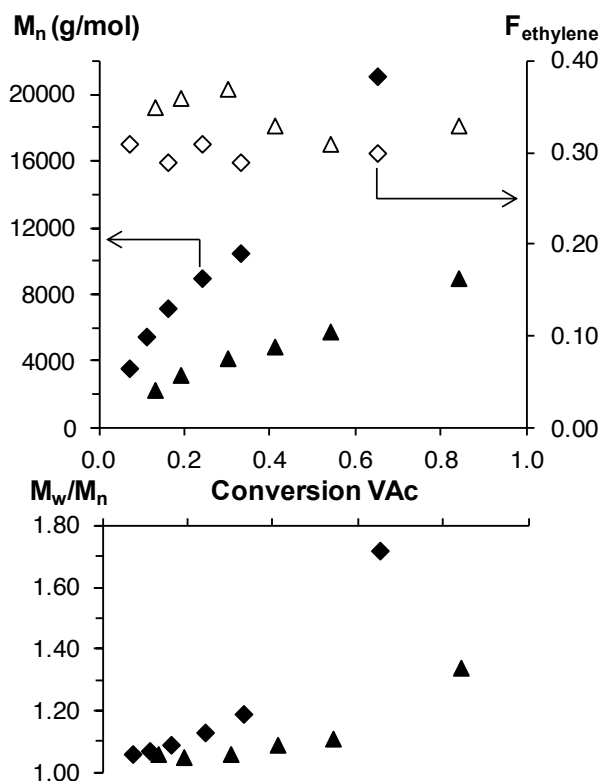


**Figure 1.** Selected size exclusion chromatograms for EVA kinetic experiments. Conditions: 40 °C, amount of Co-R:  $4.0 \cdot 10^{-4}$  mol, VAc/Co: 100,  $M_n$  and  $M_w/M_n$  measured by SEC-THF using calibration PS, VAc conversion determined by  $^1\text{H}$  NMR.

**a) EVA<sub>10 bar</sub>** ( $P_{\text{ethylene}} = 10$  bar) : 1 h)  $M_n = 1200$  g/mol,  $M_w/M_n = 1.12$ , VAc conv. = 9%; 3 h)  $M_n = 2250$  g/mol,  $M_w/M_n = 1.15$ , VAc conv. = 19%; 5 h)  $M_n = 3700$  g/mol,  $M_w/M_n = 1.07$ , VAc conv. = 35%; 9 h)  $M_n = 5500$  g/mol,  $M_w/M_n = 1.09$ , VAc conv. = 82%; 24 h)  $M_n = 8000$  g/mol,  $M_w/M_n = 1.18$ , VAc conv. = 95%.

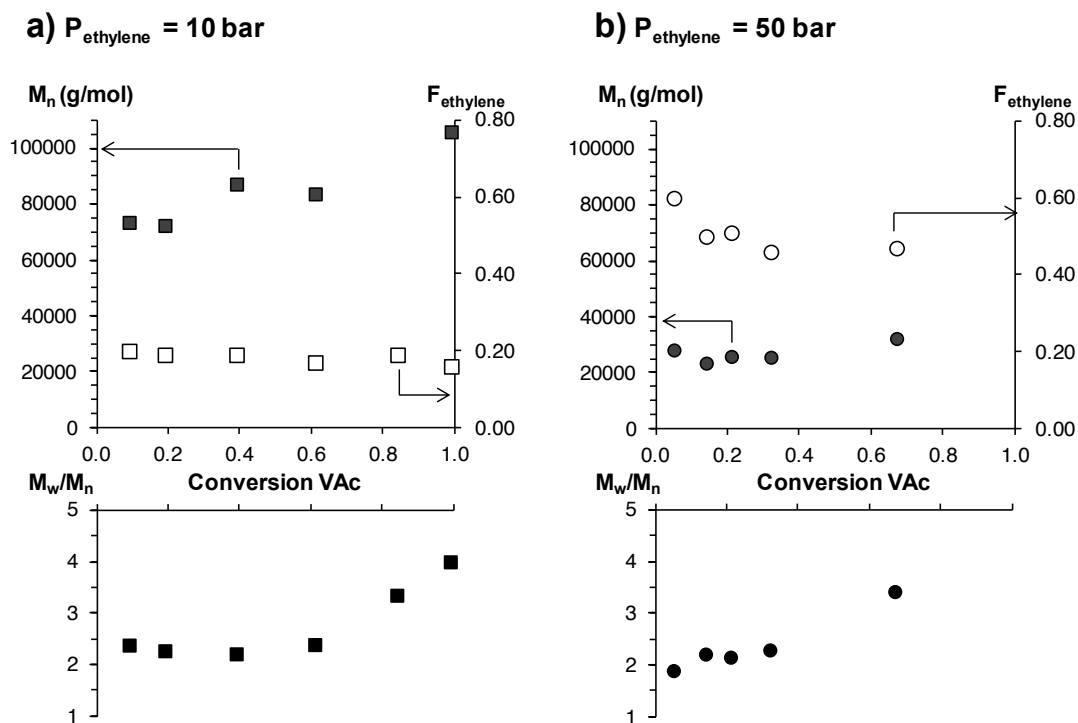
**b) EVA<sub>25 bar</sub>** ( $P_{\text{ethylene}} = 25$  bar) : 2 h)  $M_n = 2300$  g/mol,  $M_w/M_n = 1.06$ , VAc conv. = 13%; 6 h)  $M_n = 4200$  g/mol,  $M_w/M_n = 1.06$ , VAc conv. = 30%; 10 h)  $M_n = 5800$  g/mol,  $M_w/M_n = 1.11$ , VAc conv. = 54%; 24 h)  $M_n = 9000$  g/mol,  $M_w/M_n = 1.34$ , VAc conv. = 84%.

**c) EVA<sub>50 bar</sub>** ( $P_{\text{ethylene}} = 50$  bar) : 4 h)  $M_n = 2700$  g/mol,  $M_w/M_n = 1.14$ , VAc conv. = 12%; 8 h)  $M_n = 4000$  g/mol,  $M_w/M_n = 1.16$ , VAc conv. = 30%; 24 h)  $M_n = 5900$  g/mol,  $M_w/M_n = 1.32$ , VAc conv. = 66%; 48 h)  $M_n = 9700$  g/mol,  $M_w/M_n = 1.39$ , VAc conv. = 90%.



**Figure 2.** Dependence of EVA molar mass ( $M_n$ , full symbols), ethylene incorporation ( $F_{\text{ethylene}}$ , hollow symbols) and molar mass distribution ( $M_w/M_n$ , full symbols) on VAc conversion for copolymerization of VAc under 25 bar with VAc/Co-R ratio of 100 (▲) and 400 (◆); conditions: 40 °C, amount of Co-R:  $4.0 \cdot 10^{-4}$  mol, VAc/R-Co: 100 and 400, 500 rpm, ethylene pressure constant during polymerization,  $M_n$  and  $M_w/M_n$  measured by SEC-THF using a PS calibration, VAc conversion determined by  $^1\text{H}$  NMR.



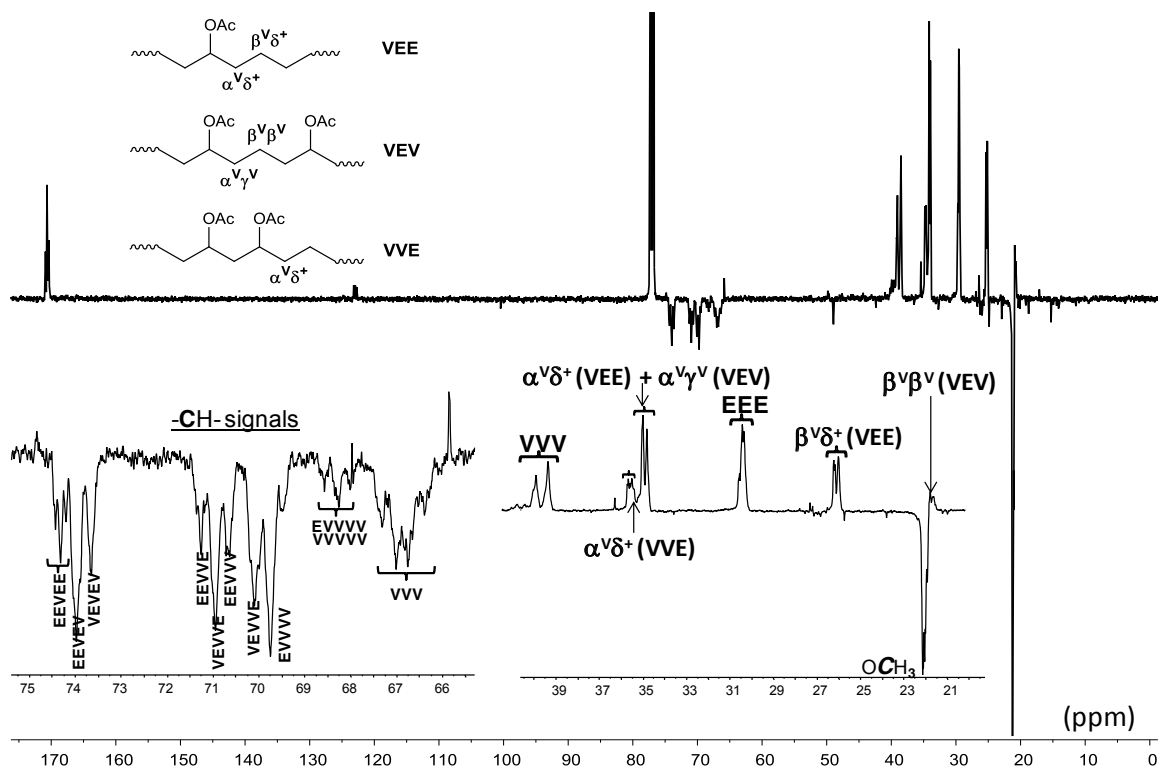


**Figure 3.** Dependence of EVA molar mass ( $M_n$ , full symbols), ethylene incorporation ( $F_{\text{ethylene}}$ , hollow symbols) and molar mass distribution ( $M_w/M_n$ , full symbols) on VAc conversion for copolymerization of VAc initiated by V70 under 10 bar (a, left, ■) and 50 bar (b, right, ●); conditions: 40 °C, amount of V70:  $2.0 \cdot 10^{-4}$  mol, VAc/V70: 100, 500 rpm, ethylene pressure constant during polymerization,  $M_n$  and  $M_w/M_n$  measured by SEC-THF using a PS calibration, VAc conversion determined by  $^1\text{H}$  NMR.

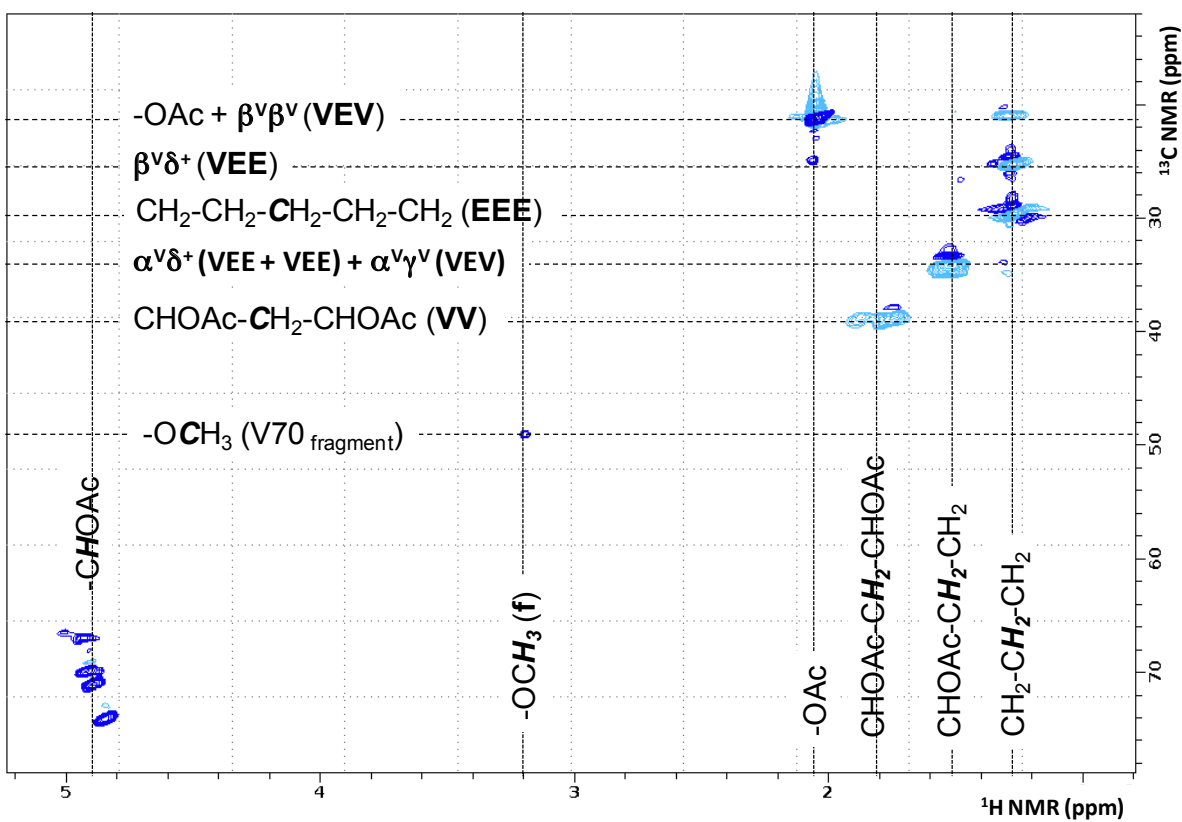
## 5- NMR characterizations

### 5.1. EVA copolymers

$^1\text{H}$ -NMR and  $^{13}\text{C}$  NMR of EVA copolymers are fully described in the article.

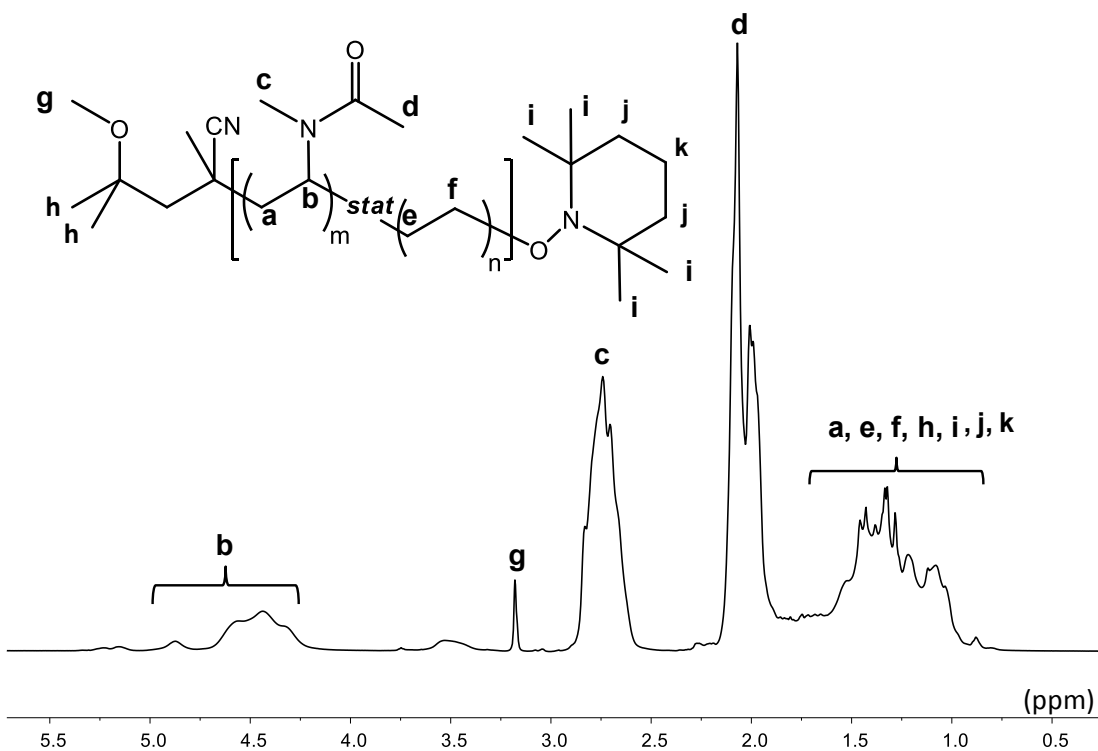


**Figure 4.** DEPTQ NMR spectrum of EVA<sub>50 bar</sub> copolymer in CDCl<sub>3</sub>.



**Figure 5.** HSQC NMR spectrum of EVA<sub>50 bar</sub> copolymer in CDCl<sub>3</sub>.

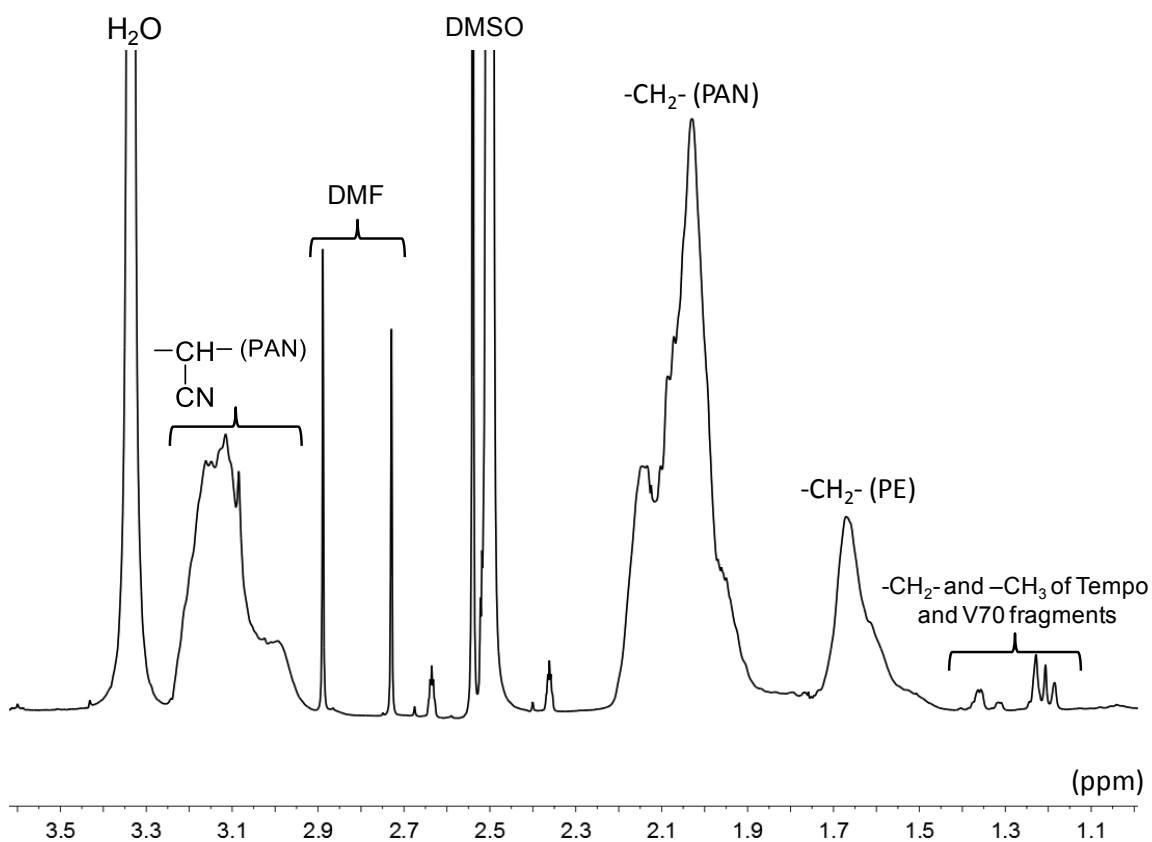
## 5.2. ENMVA copolymers



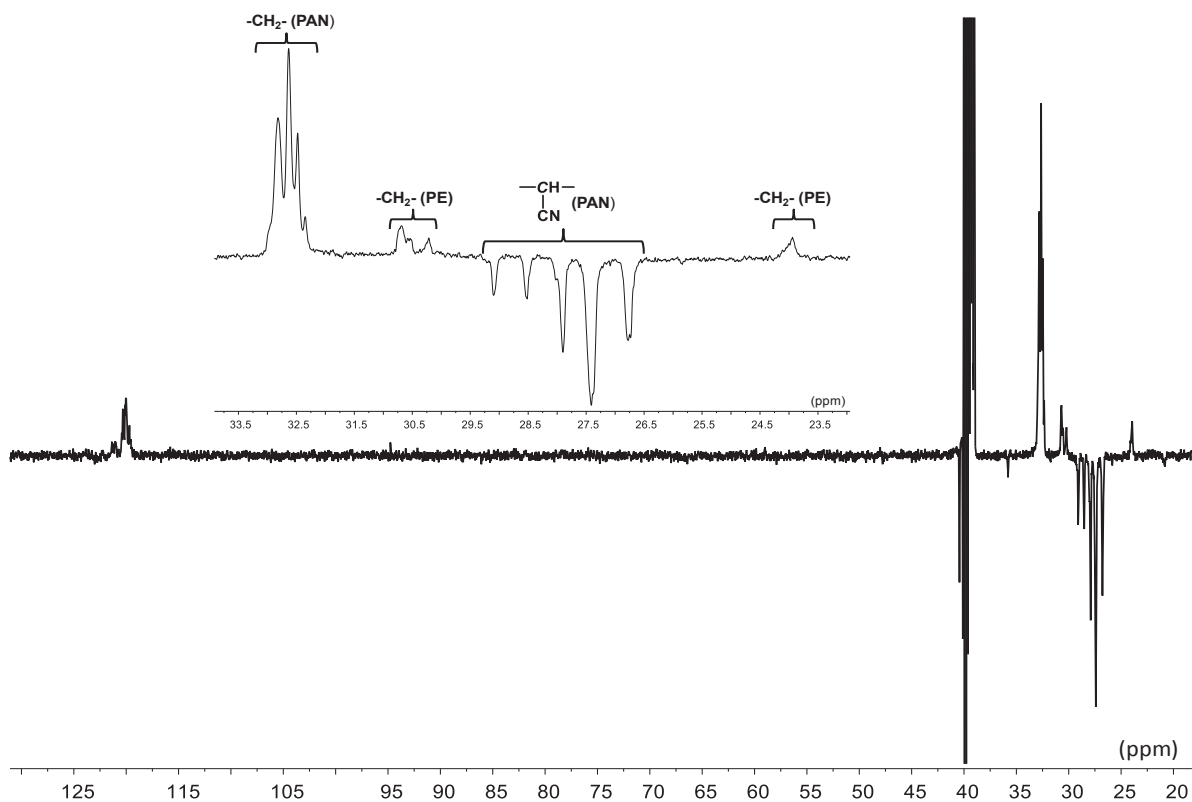
**Figure 6.** <sup>1</sup>H NMR spectrum of E/MMVA<sub>50 bar</sub> copolymer in CDCl<sub>3</sub>.

### 5.3. EAN copolymers

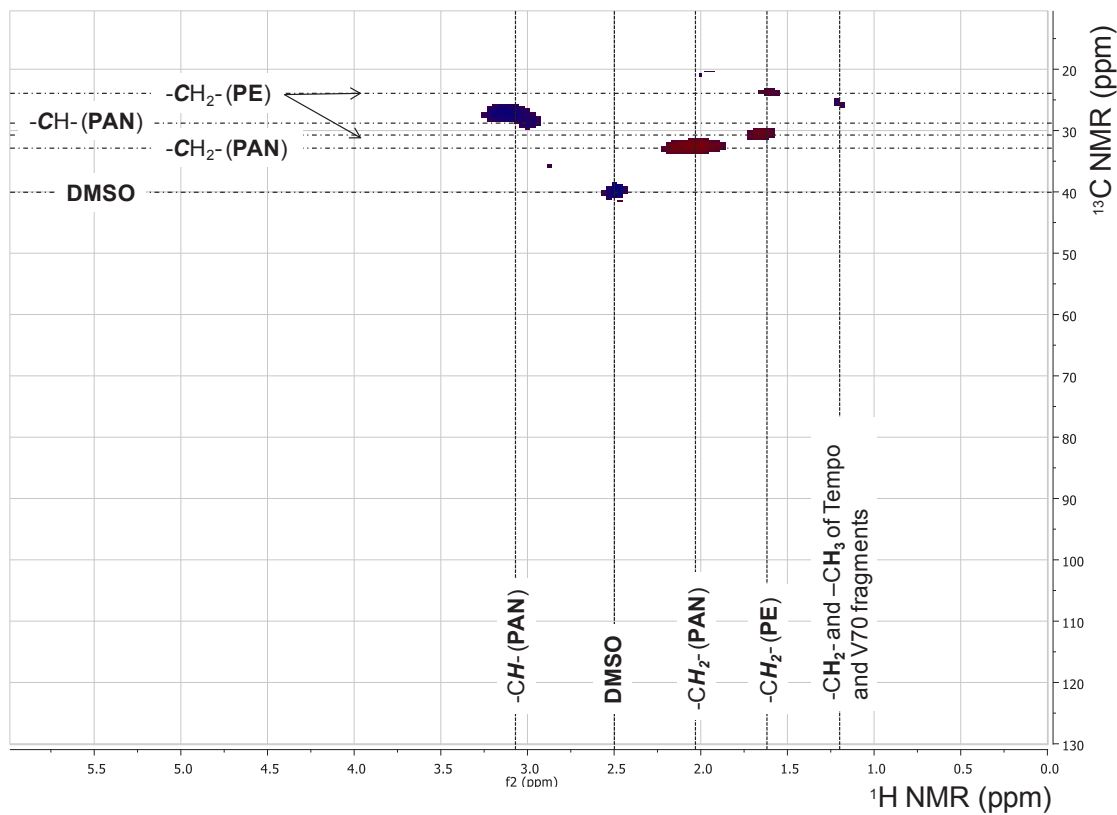
Proton NMR spectrum of EAN<sub>50 bar</sub> (Supplementary, Fig. 7) presents a broad signal centered at 1.6 ppm attributed to  $-\text{CH}_2-$  groups of incorporated ethylene units.<sup>5,6</sup> DEPTQ NMR signals centered at 24 and 30.5 ppm (Supplementary, Fig. 8) are assigned to  $-\text{CH}_2-$  species of incorporated ethylene units, according to their correlation with  $^1\text{H}$  NMR signal at 1.6 ppm observed on HSQC spectrum (Supplementary, Fig. 9).



**Figure 7.**  $^1\text{H}$  NMR spectrum of E/AN<sub>50 bar</sub> copolymer in DMSO.

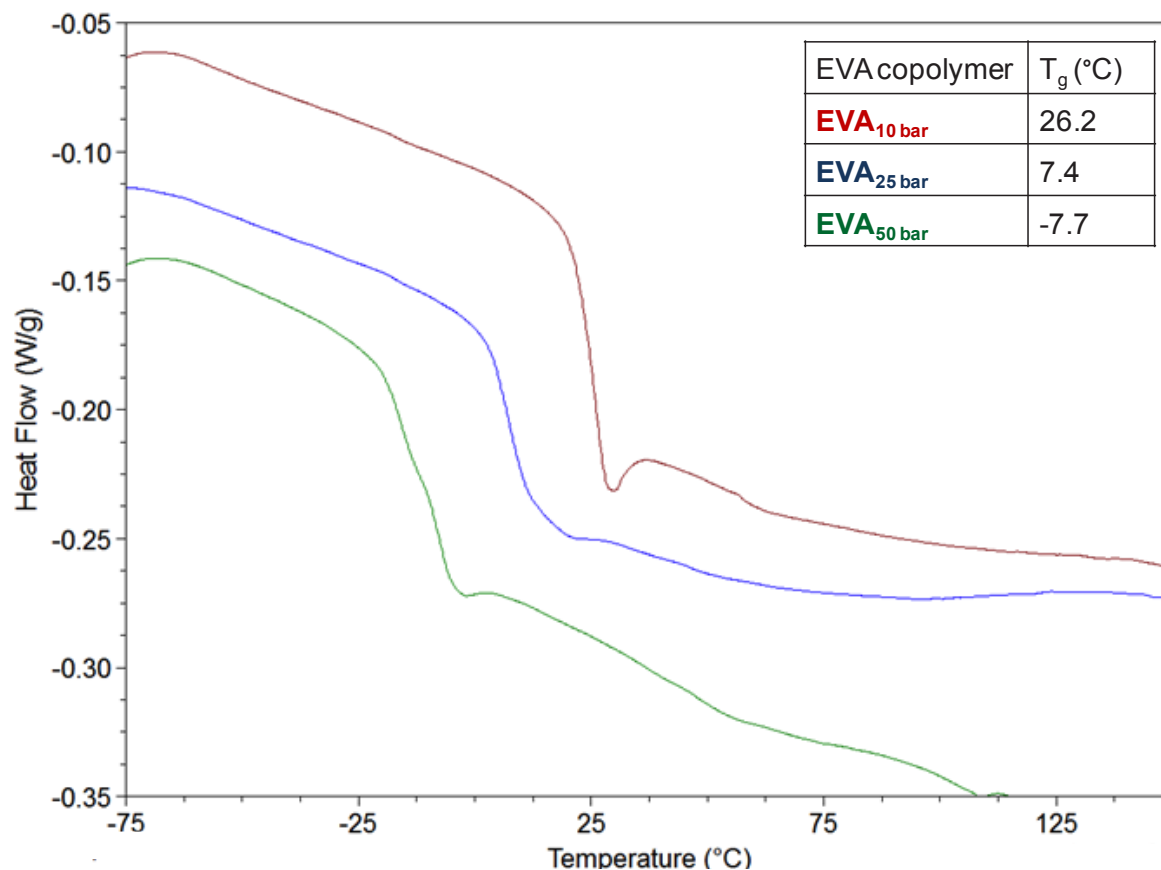


**Figure 8.** DEPTQ NMR spectrum of E/AN<sub>50</sub> bar copolymer in DMSO.



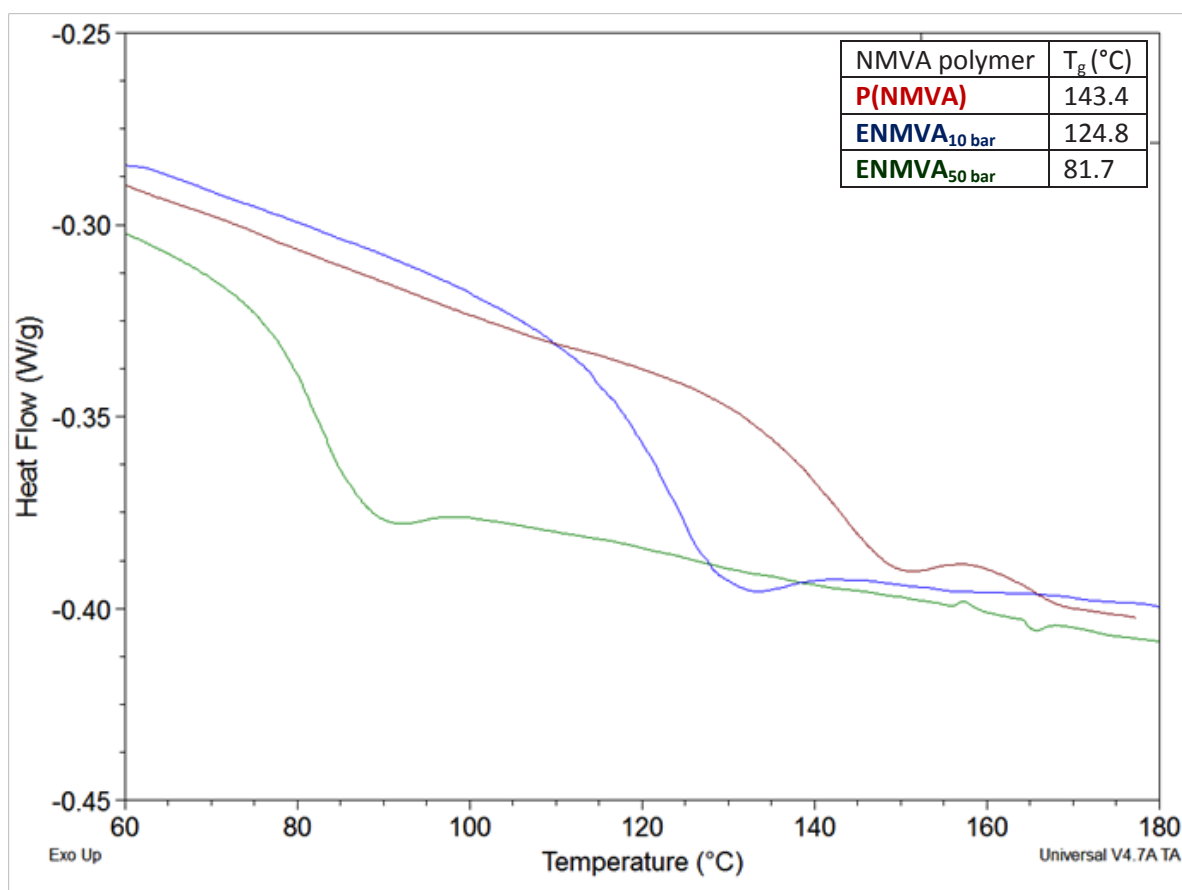
**Figure 9.** HSQC NMR spectrum of EAN<sub>50</sub> bar copolymer in DMSO.

## 6- Differential scanning calorimetry curves of copolymers



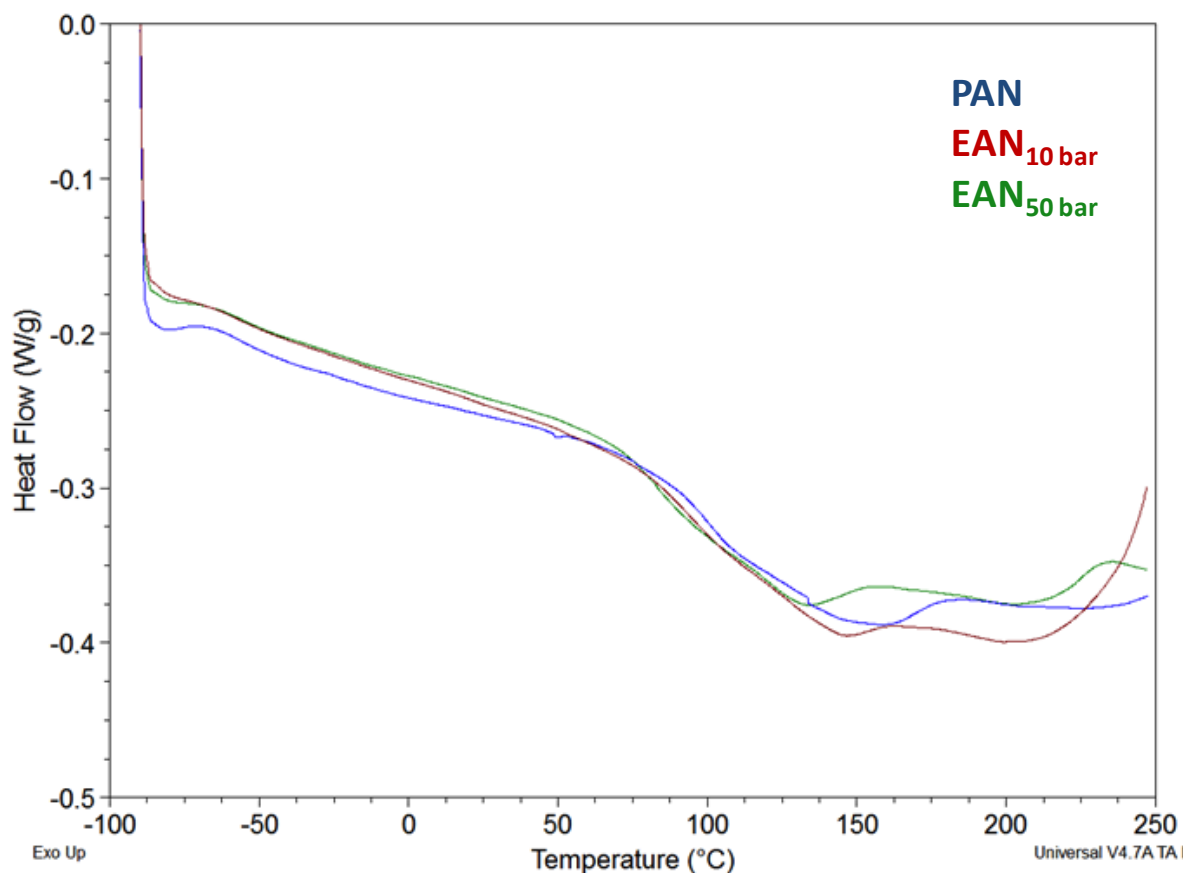
**Figure 10.** Differential scanning calorimetry curves of EVA<sub>10 bar</sub> (red), EVA<sub>25 bar</sub> (blue), EVA<sub>50 bar</sub> (green) (see Table 1 entry 1 for the macromolecular parameters of the samples).

$T_g$  values of EVA<sub>10 bar</sub>, EVA<sub>25 bar</sub> and EVA<sub>50 bar</sub> are 26.2, 7.4 and -7.7 °C, respectively and show the effect of incorporated ethylene concentrations on the thermal properties of the copolymers. These values are close to those reported in the literature for random EVA copolymers synthesized by free radical polymerization<sup>7</sup> and far from  $T_g$  of EVA copolymers produced in large scale under hard conditions (high temperature and high pressure) which are leveled to -25 °C when VAc contents are lower than 50 mol%.<sup>8</sup> Additionally  $T_g$  values of EVA initiated by V70 (30.2 and -12.4 °C under 10 or 50 bar, respectively) are in the same range of EVA initiated by R-Co. According to the Flory-Fox equation<sup>9</sup> using a  $T_g$  of -110 °C for PE, the theoretical  $T_g$  values of EVA<sub>10 bar</sub> (5 wt% of E), EVA<sub>25 bar</sub> (14 wt% of E) and EVA<sub>50 bar</sub> (28 wt% of E) are 19, -1 and -28 °C, respectively, but according to Mori et al., the Flory-Fox equation is not suitable to predict  $T_g$  of random EVA.<sup>7</sup>



**Figure 11.** Differential scanning calorimetry curves of P(NMVA) (red), ENMVA<sub>10 bar</sub> (blue), ENMVA<sub>50 bar</sub> (green) (macromolecular parameters of ENMVA are summarized in Table 1, entry 2;  $M_n$  P(NMVA) = 20100 g/mol;  $M_w/M_n$  P(NMVA) = 1.72).

$T_g$  values of ENMVA<sub>10 bar</sub> and ENMVA<sub>50 bar</sub> are 124.8 and 81.7 °C, respectively and show the effect of incorporated ethylene concentrations on the thermal properties of the copolymers as observed for EVA. This is confirmed by a  $T_g$  of 143.4 °C for a P(NMVA) (synthesized by CMRP following a previously reported procedure<sup>4</sup>) that is close to that one reported in the literature (148.3 °C).<sup>10</sup> According to the Flory-Fox equation<sup>9</sup> using a  $T_g$  of -110 °C for PE, the theoretical  $T_g$  values of ENMVA<sub>10 bar</sub> (5 wt% of E) and ENMVA<sub>50 bar</sub> (22 wt% of E) are 115 and 40 °C, respectively, but the relevance between Flory-Fox  $T_g$  and ENMVA experimental  $T_g$  must be verified with more experimental data.



**Figure 12.** Differential scanning calorimetry curves of polyacrylonitrile (PAN) (red), EAN<sub>10 bar</sub> (blue), EAN<sub>50 bar</sub> (green). (macromolecular parameters of EAN are summarized in Table 1, entry 3;  $M_{n\text{ PAN}} = 75400$  g/mol;  $M_w/M_{n\text{ PAN}} = 1.51$ ).

DSC curves of EAN<sub>10 bar</sub> and EAN<sub>50 bar</sub> show a broad transition region which can not be certainly assigned to a  $T_g$ . Indeed P(AN) polymers present complex thermal properties<sup>11</sup> and a PAN polymer (synthesized by CMRP following a previously reported procedure<sup>6</sup>) presents a similar broad transition and indicates no significant effect of ethylene incorporation on the thermal properties of the copolymers. It is certainly due to the low ethylene content in the copolymer (see Table 1, entry 3).



## 7- ESR experiments

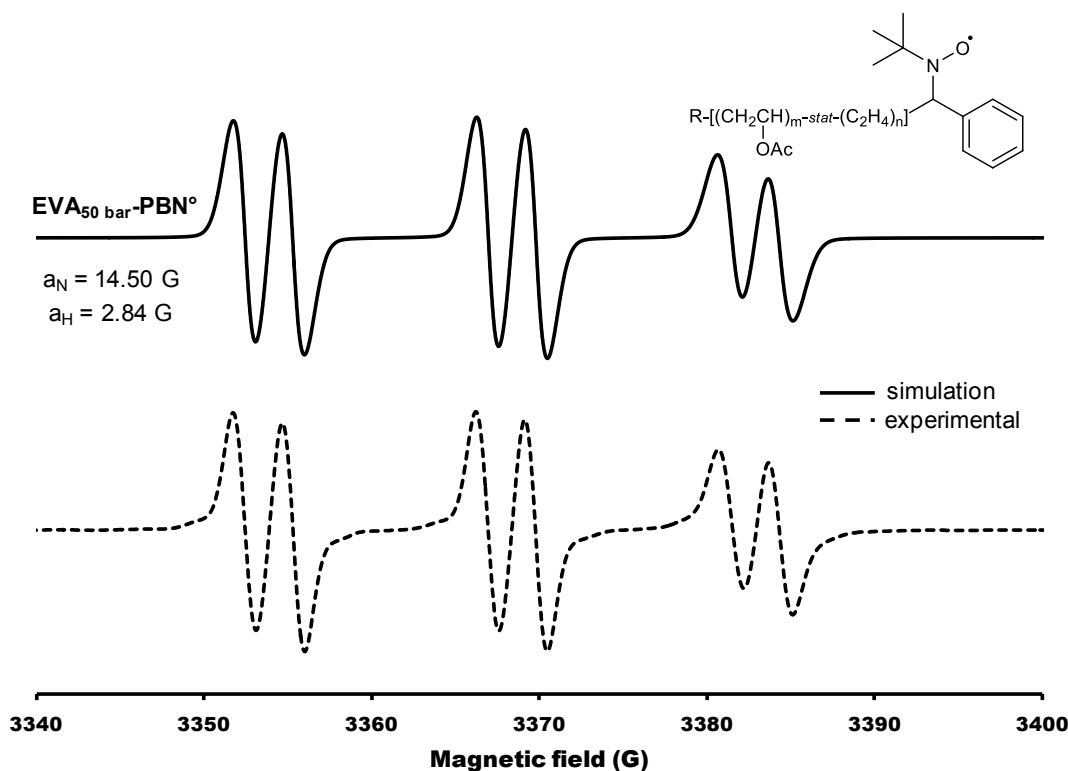
### 7.1. Spin-trapping of organo radicals coming from the decomposition of R-Co by PBN (formation of $R_0\text{-}((\text{CH}(\text{OCOCH}_3)\text{CH}_2)_{<4})\text{-PBN}\bullet$ )

A solution of organo-cobalt(III) initiator  $[\text{Co}(\text{acac})_2\text{-}(\text{CH}(\text{OCOCH}_3)\text{CH}_2)_{<4}\text{-R}_0]$  in  $\text{CH}_2\text{Cl}_2$  (1.0 mL of a 0.064 M stock solution,  $6.4 \times 10^{-5}$  mol) was introduced under argon in a 30 mL Schlenk and evaporated to dryness under reduced pressure at room temperature. A solution of PBN (34 mg,  $1.9 \times 10^{-4}$  mol) in 10 mL of degassed tert-butylbenzene was then added and reacted for 10 min at 40 °C. The resulting solution was analyzed by ESR (Figure 5) under argon (volume of ESR solution: 0.12 mL) at 25 °C.

### 7.2. Spin-trapping of EVA radical by PBN (formation of $\text{EVA}_{50 \text{ bar}}\text{-PBN}\bullet$ )

A solution of organo-cobalt(III) initiator  $[\text{Co}(\text{acac})_2\text{-}(\text{CH}(\text{OCOCH}_3)\text{CH}_2)_{<4}\text{-R}_0]$  (2.0 mL of a 0.064 M stock solution in  $\text{CH}_2\text{Cl}_2$ ,  $1.3 \times 10^{-4}$  mol) was introduced under argon in a 30 mL Schlenk tube and evaporated to dryness under reduced pressure at room temperature. A volume of VAc (1.2 mL,  $1.3 \times 10^{-2}$  mol) was added under argon and the solution was then transferred into a 30 mL stainless steel TopIndustrie autoclave under an ethylene atmosphere using a cannula. The autoclave was pressurized at 50 bar of ethylene and heated at 40 °C using an oil bath. The pressure was manually maintained during the polymerization and the reaction mixture was magnetically stirred at 500 rpm. After 6 h of reaction, ethylene was removed and the solution was transferred via a cannula into a schlenk containing a solution of PBN (68 mg,  $3.8 \times 10^{-4}$  mol) in 10 mL of degassed tert-Butylbenzene and reacted for 10 min at 40 °C. An aliquot was picked out the medium to determine the VAc conversion by  $^1\text{H}$  NMR spectroscopy in  $\text{CDCl}_3$  and the molecular parameters of the copolymer by SEC in THF. A volume of 0.12 mL was analyzed by ESR under argon at 25 °C (Supplementary, Fig. 13).

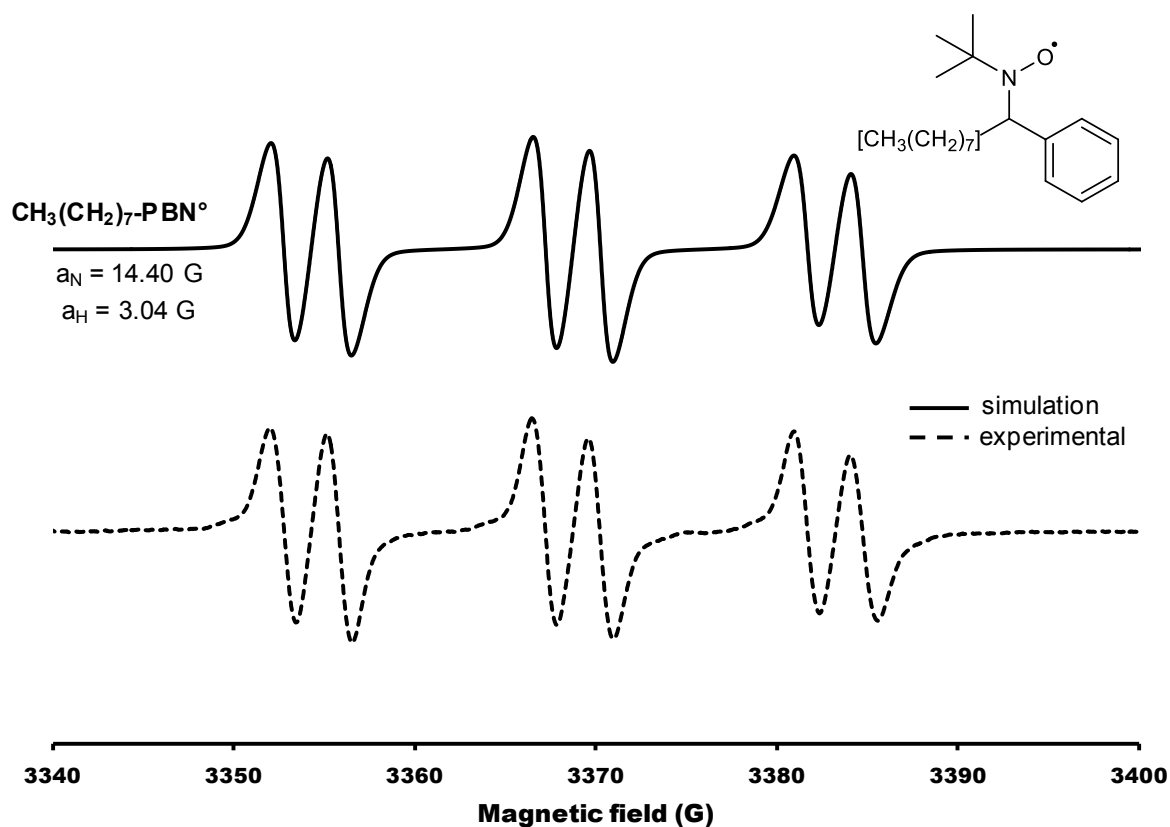
After 6 h: VAc conversion of 18 %,  $F_{\text{ethylene}} = 0.45$  (determined by  $^1\text{H}$  NMR),  $M_n = 3000$  g/mol;  $M_w/M_n = 1.12$  (GPC-THF, cal. PS).



**Figure 13.** Simulated (top) and experimental (bottom) ESR spectra of EVA<sub>50</sub> bar-PBN<sup>•</sup> (polymerization time of 6 h) in tert-butylbenzene at 25 °C.

### 7.3. Spin-trapping of octyl radical by PBN (formation of CH<sub>3</sub>-(CH<sub>2</sub>)<sub>7</sub>-PBN<sup>•</sup>)<sup>12</sup>

Sodium (0.010 g, 0.4 mmol) was added into a schlenk containing a solution of PBN (0.106 g, 0.6 mmol) and bromooctane (0.116 g, 0.6 mmol) in 10 mL of dry hexane under argon and reacted for 1 h at room temperature. Then the solution was transferred into a second schlenk (to separate Na) and all volatiles are removed under reduced pressure. Degassed tert-Butylbenzene (10 mL) was added and the resulting solution was analyzed by ESR (Supplementary, Fig. 14) under argon (volume of ESR solution: 0.12 mL) at 25 °C.



**Figure 14.** Simulated (top) and experimental (bottom) ESR spectra of  $\text{CH}_3\text{-(CH}_2\text{)}_7\text{-PBN}^\bullet$  in tert-Butylbenzene at 25 °C.

#### 7.4. Spin-trapping of $\text{R-(C}_2\text{H}_4\text{)}_n$ radical by PBN (formation of $\text{R-(C}_2\text{H}_4\text{)}_n\text{-PBN}^\bullet$ )

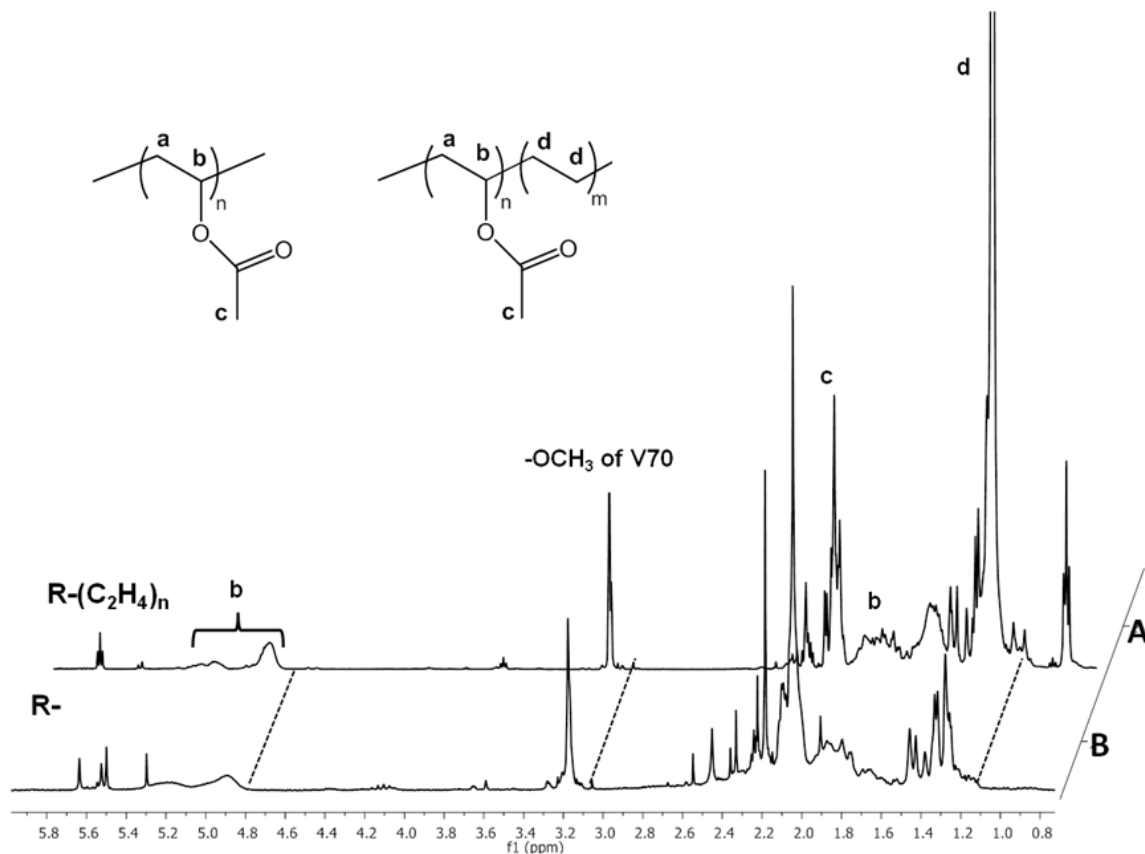
A solution of organo-cobalt(III) initiator [ $\text{Co}(\text{acac})_2\text{-(CH(OCOCH}_3\text{)CH}_2\text{)}_{<4\text{-R}_0}$ ] in  $\text{CH}_2\text{Cl}_2$  (1.0 mL of a 0.064 M stock solution,  $6.4 \times 10^{-5}$  mol) was introduced into a 30 mL stainless steel TopIndustrie autoclave under an ethylene atmosphere. The autoclave was pressurized at 50 bar by ethylene and heated at 40 °C using an oil bath. The pressure was manually maintained during the polymerization and the reaction mixture was magnetically stirred at 500 rpm. After 20 h of reaction, ethylene was removed and the solution was evaporated to dryness under reduced pressure at room temperature. A solution of PBN (34 mg,  $1.9 \times 10^{-4}$  mol) in 10 mL of degassed tert-butylbenzene was transferred via a cannula into the autoclave under argon and reacted for 10 min at 40 °C. The resulting solution was analyzed by ESR (Supplementary, Fig. 13) under argon (volume of ESR solution: 0.12 mL) at 25 °C.

**8- Attempt to homopolymerize ethylene and characterization of the product (R-(C<sub>2</sub>H<sub>4</sub>)<sub>n</sub>)**

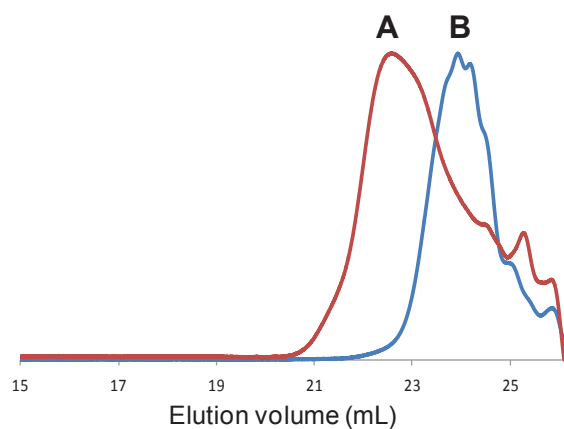
A solution of organo-cobalt(III) initiator [Co(acac)<sub>2</sub>-(CH(OCOCH<sub>3</sub>)CH<sub>2</sub>)<sub>4</sub>-R<sub>0</sub>] in CH<sub>2</sub>Cl<sub>2</sub> (8.0 mL of a 0.064 M stock solution, 5.1 × 10<sup>-4</sup> mol) was introduced into a 30 mL stainless steel TopIndustrie autoclave under an ethylene atmosphere. The autoclave was pressurized at 50 bar by ethylene and heated at 40 °C using an oil bath. The pressure was manually maintained during the polymerization and the reaction mixture was magnetically stirred at 500 rpm. After 20 h of reaction, the autoclave was depressurized and a TEMPO solution (0.1 g, 6.4 × 10<sup>-4</sup> mol) in 5 mL of degassed THF was introduced under argon and reacted for 30 min at room temperature to stop the reaction.<sup>4</sup> The solution was evaporated to dryness and dissolved in 2 mL of CHCl<sub>3</sub>. The compound was purified by flash chromatography (SiO<sub>2</sub>, 10 cm) using CHCl<sub>3</sub> as eluent. A first pale red fraction containing the expected product (R-(C<sub>2</sub>H<sub>4</sub>)<sub>n</sub>; 62 mg) was collected whereas a second pale green fraction containing deactivated organo-cobalt(III) initiator (125 mg) was separated later. Unreacted TEMPO and Co residues were remaining on the column.

The first fraction (R-(C<sub>2</sub>H<sub>4</sub>)<sub>n</sub>) was analyzed by <sup>1</sup>H NMR in CDCl<sub>3</sub> (Supplementary, Fig. 15A). The presence of incorporated ethylene units is clearly shown with signal centered at 1.25 ppm assigned to the CH<sub>2</sub> repeating units of ethylene and not observed on the <sup>1</sup>H NMR spectrum of R- (R-Co treated with TEMPO, noted R- in Supplementary, Fig. 15B).<sup>1</sup> The incorporation of approximately 14 ethylene units was evaluated by integration of the signal at 1.25 ppm and integration of OCH<sub>3</sub> signal of V70 fragment (one OCH<sub>3</sub> groups corresponds to one polymer chain, Figure 3).

Molecular parameters of R-(C<sub>2</sub>H<sub>4</sub>)<sub>n</sub> were determined by SEC-THF using a PS calibration (M<sub>n</sub> = 900 g/mol, M<sub>w</sub>/M<sub>n</sub> = 1.54, Supplementary, Fig. 16A) and showed a slight increase of M<sub>n</sub> compared to R-Co treated with a TEMPO solution (M<sub>n</sub> = 700 g/mol, M<sub>w</sub>/M<sub>n</sub> = 1.17, Supplementary, Fig. 16B). This is an additional evidence of addition of few ethylene molecules on R-Co initiator.



**Figure 15.**  $^1\text{H}$  NMR spectra of  $\text{R}-(\text{C}_2\text{H}_4)_{14}$  (A) and  $\text{R}-$  (B) in  $\text{CDCl}_3$  (R- from R-Co initiator).



**Figure 16.** Size exclusion chromatograms in THF (PS calibration) for (A)  $\text{R}-(\text{C}_2\text{H}_4)_{14}$  ( $M_n = 900$  g/mol,  $M_w/M_n = 1.54$ ) and (B)  $\text{R}-$  (PVAc oligomers,  $M_n = 700$  g/mol,  $M_w/M_n = 1.17$ ).

## 9- Supplementary Tables

**Table 1.** ABA triblock copolymers ((EVA<sub>50bar</sub>)-*b*-(EVA<sub>10bar</sub>)<sub>2</sub>-*b*-(EVA<sub>50bar</sub>)) resulting from the block copolymerization of VAc and ethylene at 40 °C ((EVA<sub>50bar</sub>)-*b*-(EVA<sub>10bar</sub>)), followed by coupling with isoprene.

Block	Pressure (bar)	Time (h)	Conv. VAc(%) <sup>d</sup>	M <sub>n</sub> <sup>e</sup> (g/mol)	M <sub>w</sub> /M <sub>n</sub> <sup>e</sup>	M <sub>p</sub> <sup>e</sup> (g/mol)	Composition <sup>d</sup>	
							F <sub>VAc</sub>	F <sub>ethylene</sub>
First <sup>a</sup>	50	5	14	4300	1.12	4800	48	52
Second <sup>b</sup>	10	5	27	5000	1.14	5900	52	48
Coupling <sup>c</sup>	-	-	-	9800	1.20	12200	57	43

<sup>a</sup> First block synthesized by CMRP initiated with  $4.0 \cdot 10^{-4}$  mol of R-Co (VAc/Co ratio of 100). <sup>b</sup> Second block synthesized after pressurization of reactor to 10 bar. <sup>c</sup> coupling in the presence of 2 mL of isoprene (isoprene/Co: 50). <sup>d</sup> determined by <sup>1</sup>H NMR. <sup>e</sup> THF-GPC using PS calibration.

**Table 2.** ABA triblock copolymers ((EVA<sub>10bar</sub>)-*b*-(EVA<sub>50bar</sub>)<sub>2</sub>-*b*-(EVA<sub>10bar</sub>)) resulting from the polymerization of VAc and ethylene at 40 °C ((EVA<sub>10bar</sub>)-*b*-(EVA<sub>50bar</sub>)), followed by isoprene coupling.

Block	Pressure (bar)	Time (h)	Conv. VAc(%) <sup>d</sup>	M <sub>n</sub> <sup>e</sup> (g/mol)	M <sub>w</sub> /M <sub>n</sub> <sup>e</sup>	M <sub>p</sub> <sup>e</sup> (g/mol)	Composition <sup>d</sup>	
							F <sub>VAc</sub>	F <sub>ethylene</sub>
First <sup>a</sup>	10	5	31	3450	1.05	3700	79	21
Second <sup>b</sup>	50	5	55	5800	1.14	6700	64	36
Coupling <sup>c</sup>	-	-	-	8400	1.33	13400	63	37

<sup>a</sup> First block synthesized by CMRP initiated with  $4 \cdot 10^{-4}$  mol of R-Co (VAc/Co ratio of 100). <sup>b</sup> Second block synthesized after pressurization of reactor to 50 bar. <sup>c</sup> coupling in the presence of 2 mL of isoprene (isoprene/Co: 50). <sup>d</sup> determined by <sup>1</sup>H NMR. <sup>e</sup> THF-GPC using PS calibration.

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