Supporting Information to:

Poly(vinyl acetate-*co*-ethylene) particles prepared by surfactant-free emulsion polymerization in the presence of a hydrophilic RAFT/MADIX macromolecular chain transfer agent.

James Delorme, Olivier Boyron, Pierre-Yves Dugas, Pierre-Emmanuel Dufils, James Wilson, Vincent Monteil, Franck D'Agosto,* Muriel Lansalot*

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1. Aqueous emulsion copolymerizations of VAc and ethylene mediated by 10, 20 and 65 wt% of P(AAm-*co*-AA)-X at 77 °C

Table S1 Batch aqueous emulsion copolymerizations of VAc and ethylene mediated by 10, 20 and 65 wt% of P(AAm-*co*-AA)-X.

Latex	macroCTA (wt%) [a]	P (bar)	SC (%) [b]	PC (%) [b]	Z_{ave} (nm) [c]	PdI [c]	VAc (wt%) [d]	VAc (mol%) [e]	X_{VAc} (%) [f]	T_g (°C) [g]	Xc (%) [h]
L7		0	9.5	8.4	134	0.08	100	100	90	42.3	-
L8		10	11.0	9.8	69	0.07	97.0	82.2	93	27.2	-
L9	10	35	11.9	10.8	75	0.14	78.1	53.7	87	3.71	-
L10		50	12.5	11.4	100	0.20	54.8	28.3	69	-33.0	-
L11		100	18.5	17.4	58	0.06	33.6	14.4	62	-28.2	13.6
L12		0	10.3	8.2	100	0.2	100	100	86	37.2	-
L13	20	10	10.1	8.1	82	0.25	97.0	84.6	81	27.4	-
L14		35	10.8	8.8	61	0.15	65.3	38.7	62	-3.9	-
L15		50	13.4	11.4	67	0.18	47.5	21.4	50	-36.8	2.7
L16		0	13.8	7.9	37	0.05	100	100	89	28.3	-
L17		10	13.8	7.8	70	0.30	N.D.	N.D.	N.D.	15.7	-
L18	65	35	14.4	8.4	82	0.44	N.D.	N.D.	N.D.	-11.2	-
L19		50	14.0	7.8	169	0.16	N.D.	N.D.	N.D.	-18.6	-
L20 [i]		100	-	-	-	-	-	-	-	-	-

For all experiments, [AcV] = 1.09 mol L^{-1}, T = 77 °C, reaction time = 4 h. [a] With respect to VAc amount. [b] Solid content (SC) and Polymer content (PC), with PC = SC – amount of non-volatile species (in %). [c] Determined by DLS. [d] Weight content and [e] molar content of VAc units in formed P(VAc-*co*-E) determined by averaging the values from the relevant analyses. [f] VAc conversion calculated from equation (1). [g] Determined by DSC. [h] Degree of crystallinity (Xc) calculated from equation (2). [i] Inconclusive experience, the polymerization did not work.
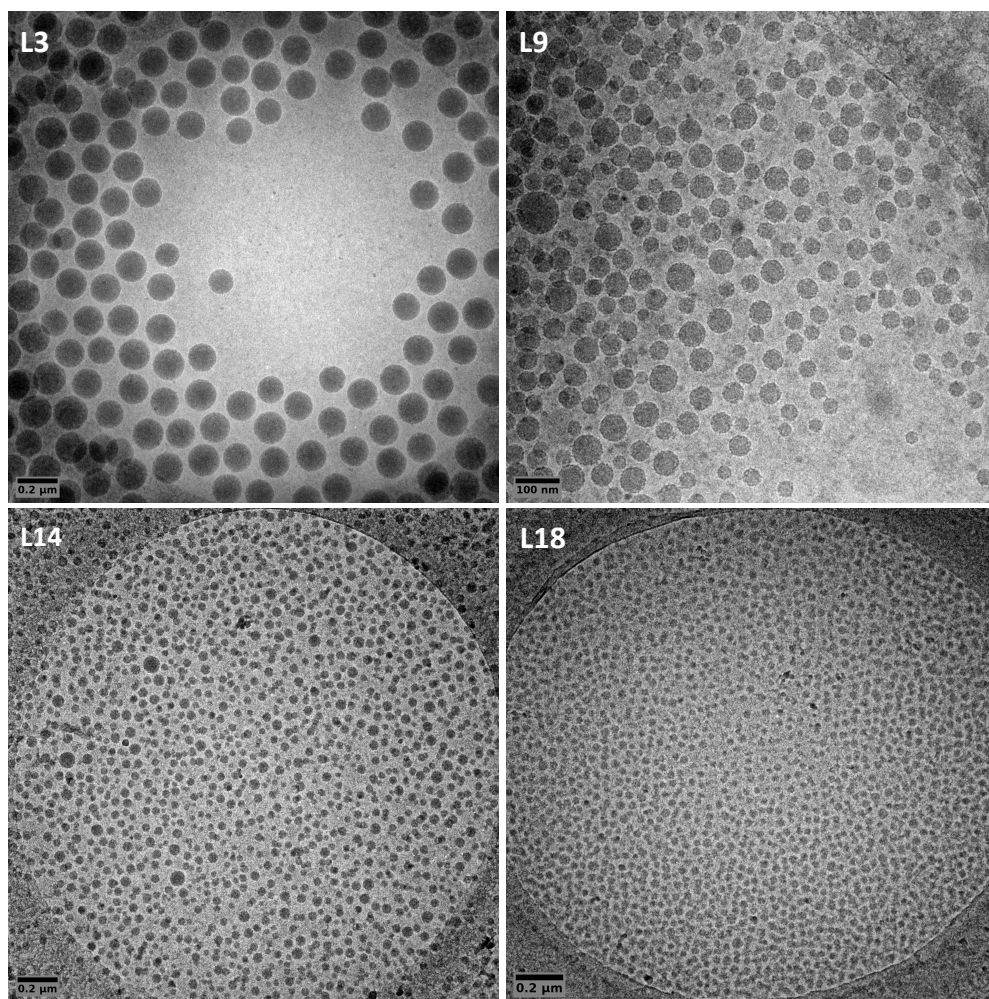
Fig. S1 Cryo-TEM images of P(VAc-*co*-E) latexes synthesized at 35 bar of ethylene pressure, using varying amount of macroCTA: 1 wt% (L3), 10 wt% (L9), 20 wt% (L14) and 65 wt% (L18)
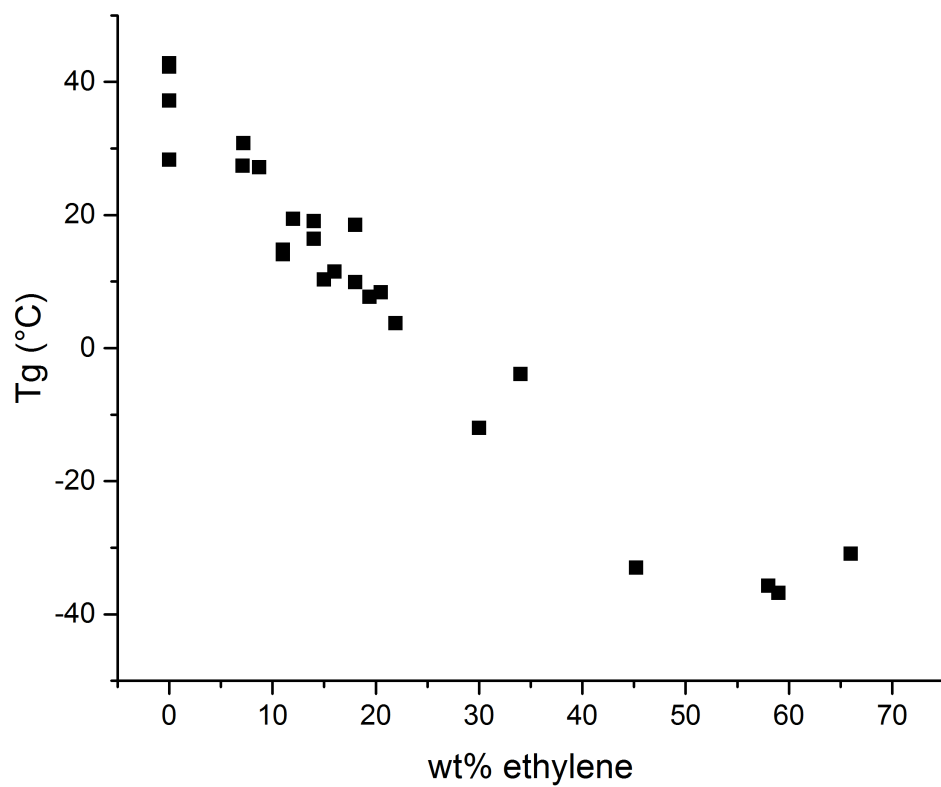
Fig. S2 Evolution of T_g versus ethylene content for all the P(VAc-*co*-E) copolymers prepared in this study.

2. Determination of the composition of P(VAc-*co*-E) copolymers

The compositions of the copolymers indicated in the different tables were determined by several techniques: NMR, FTIR, TGA and DSC. Indeed, it was not possible to dissolve the synthesized copolymers in usual EVA or VAE solvents, such as chloroform or mixture of tetracloroethylene/benzene where they rather form translucent gels. NMR analyzes in a mixture of tetrachloroethylene and deuterated benzene (volume ratio 2/1) could nevertheless be carried out on these gels giving exploitable spectra, which were used to determine the composition of the copolymer as shown below. Nevertheless, the corresponding data remain to be considered with caution. Additional characterization techniques were therefore implemented to cross-check the results and determine as precisely as possible the composition of the EVAs.

Table S2 Composition of the P(VAc-*co*-E) copolymers.

Latex	VAc, wt%				Selected technique(s)	Average value (wt%)
	DSC	NMR	TGA	Chemometry IR		
L2	100	87.2	93.0	85.8	NMR, TGA, IR	88.7
L3	85.0	80.5	80.7	80.6	NMR, TGA, IR	80.6
L4	70.0	70.0	70.0	70.0	DSC, NMR, TGA, IR	70.0
L5	41.0	41.0	45.0	39.8	DSC, NMR, TGA, IR	41.7
L6	ND	85.0	ND	ND	NMR	85.0
L3*	ND	74.5	ND	ND	NMR	74.5
L8	97.0	ND	97.0	ND	DSC, TGA	97.0
L9	83.0	77.9	72.1	74.6	DSC, NMR, TGA, IR	76.9
L10	45.0	54.8	54.9	53.5	NMR, TGA, IR	54.4
L11	50.0	33.2	34.1	33.4	NMR, TGA, IR	33.7
L13	97.0	ND	ND	ND	DSC	97.0
L14	80.0	ND	64.0	66.7	TGA, IR	65.3
L15	40.0	ND	ND	55.1	DSC, IR	47.5
L17	ND	ND	ND	ND	ND	ND
L18	ND	ND	ND	ND	ND	ND
L19	ND	ND	ND	ND	ND	ND
L20	ND	ND	ND	ND	ND	ND
L21	ND	ND	ND	ND	ND	ND
L22	ND	ND	ND	ND	ND	ND
L23	ND	ND	ND	79.5	IR	79.5
L24	95.0	ND	ND	82.0	IR	82.0
L25	90.0	ND	ND	89.0	DSC, IR	89.5
L26	85.0	ND	83.0	86.0	DSC, TGA, IR	84.7
L27	93.0	ND	85.8	90.0	TGA, IR	87.9
L28	93.0	88.0	84.0	86.0	TGA, NMR, IR	86.0
L29	ND	ND	ND	86.0	IR	86.0
L30	86.5	83.0	80.0	84.0	TGA, NMR, IR	82.3
L31	90.0	ND	ND	88.7	DSC, IR	89.3

- ***Determination of copolymer compositions by IR and chemometry.***

A multivariate calibration model was used to quantify the VAc content in our samples (Fig. S3). Three PLS factors were selected to properly describe the variables and get a correlation coefficient of 0.995. A first derivative and a Savitzky-Golay smoothing were applied to the data before the calculation to reduce the baseline offset.
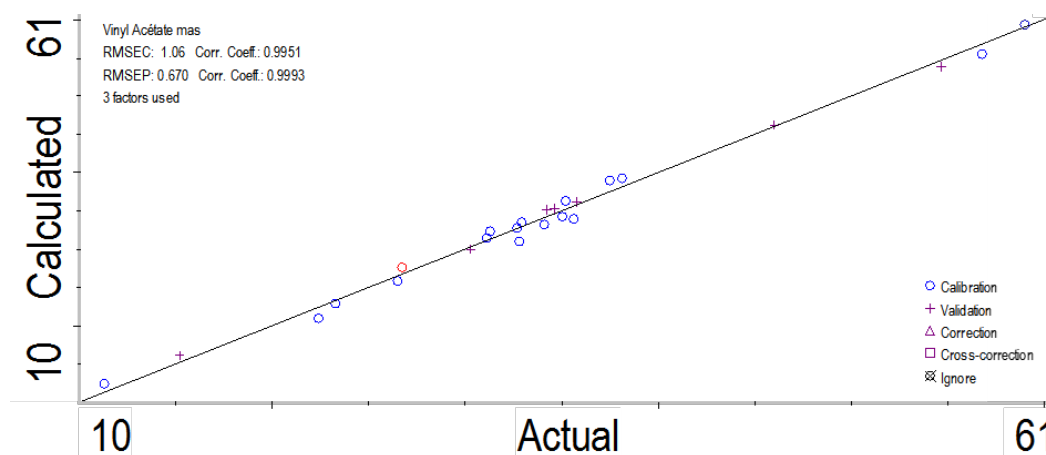

Fig. S3 Correlation diagrams between predicted and reference values of the dataset for 26 EVA copolymers (3.5 < M_n < 35 kg mol^{-1} and $Đ$ = 1.8 ± 0.3. Blue data for calibration and pink data for validation). The units of both axes are expressed in mol% (VAc content).

- ***Determination of copolymer compositions by DSC.***

The weight content of vinyl acetate in the copolymers was also determined using the T_g values obtained by DSC analyses (e.g. L5 and L11, Fig. S4) and the plot from reference 1 in Fig. S5, reporting the evolution of the weight content of vinyl acetate in various P(VAc-*co*-E) copolymers *versus* their T_g and enthalpy of fusion of ethylene.
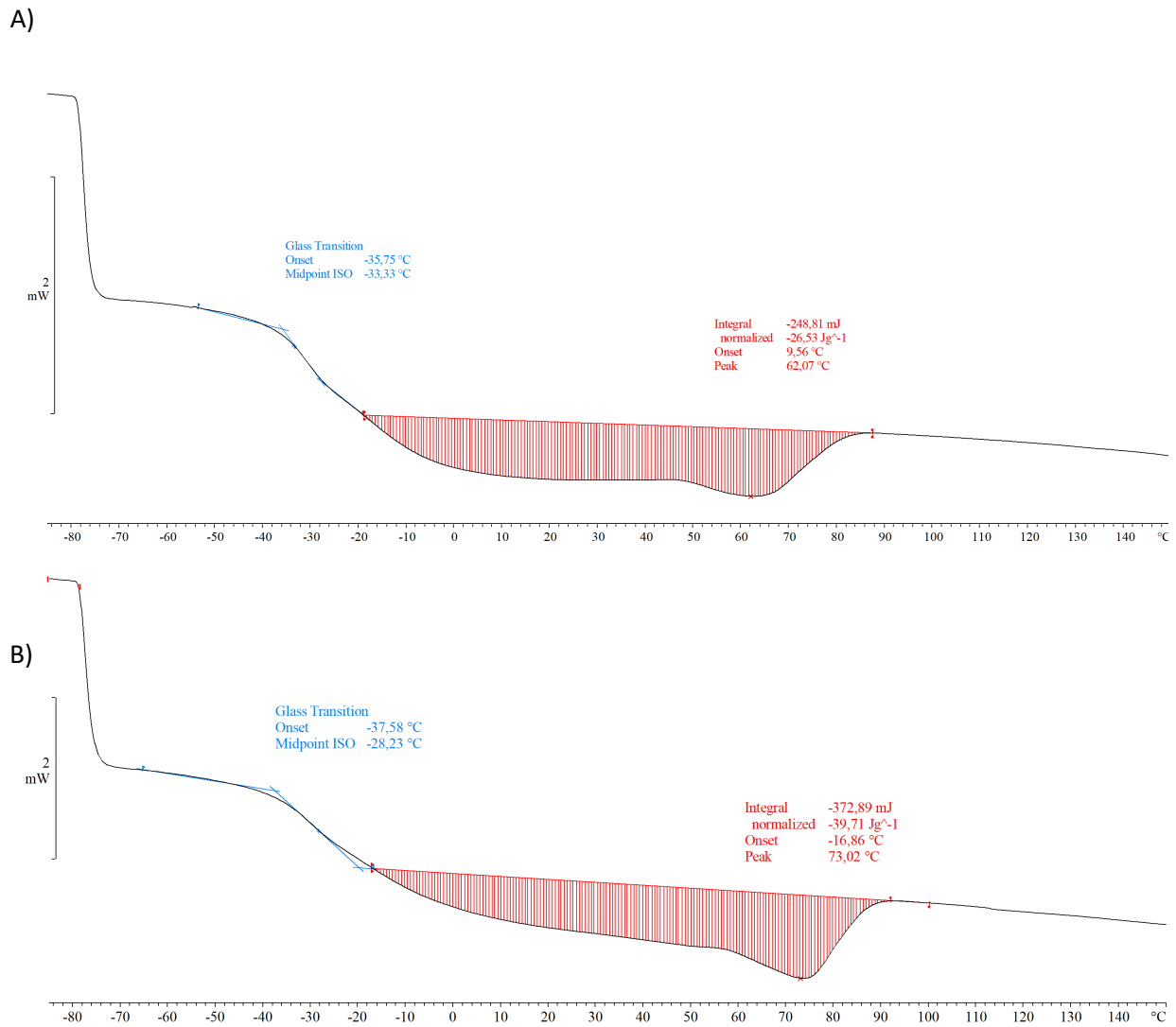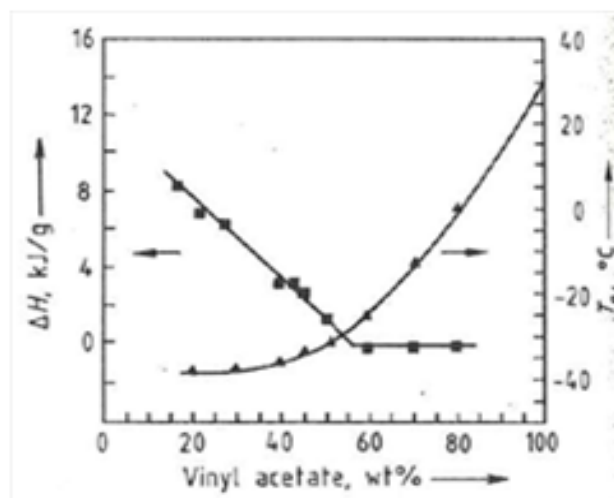
A)

Glass Transition
Onset   -35,75 °C
Midpoint ISO   -33,33 °C

Integral   -248,81 mJ
 normalized   -26,53 Jg^-1
Onset   9,56 °C
Peak   62,07 °C

B)

Glass Transition
Onset   -37,58 °C
Midpoint ISO   -28,23 °C

Integral   -372,89 mJ
 normalized   -39,71 Jg^-1
Onset   -16,86 °C
Peak   73,02 °C

Fig. S4 Examples of DSC curve of EVA with high ethylene content. A) L5 (Table 1), and B) L11 (Table S1).

Fig. S5 Evolution of the weight content of vinyl acetate in P(VAc-*co*-E) copolymers *versus* T$_g$ and enthalpy of fusion ΔH of ethylene. Adapted from reference 1.

This method has three limits that can impact the values obtained: (1) the heating rate for this calibration curve is different from ours (20 °C min^{-1} versus 10 °C min^{-1} in our case). (2) When the EVA has high ethylene content a melting peak appears (Fig. S6). It is then difficult to accurately determine the T_g value. (3) Finally, the method was set up for VAc content higher than 20%.

- ### *Determination of copolymer compositions by NMR.*

As mentioned in the main text, the copolymers were not soluble in the NMR solvents tested. However, in a mixture tetracloroethylene/deuterated benzene (generally used in our hands at high temperature to successfully solubilize analyze polyethylene samples) the synthesized poly(vinyl acetate-*co*-ethylene) form a gel at room temperature without improvement when increasing the analysis temperature. They are therefore solvated but not solubilized and can be analyzed at room temperature (Fig. S6). The molar contents in vinyl acetate (n) and ethylene (p) units were then determined using the following assignments:

Knowing the integration relative to protons a (I_a) and the integral I, the different content are thus:

$$n = \text{mol\% VAc} = 100 \times \frac{I_a}{I_a + \left(\frac{I-5I_a}{4}\right)} \qquad p = \text{mol\% E} = 1 - n = 1 - 100 \times \frac{I_a}{I_a + \left(\frac{I-5I_a}{4}\right)}$$

This technique was considered valid for VAc content comprised between 0 and 100 wt% (*i.e.* 0 and 100 mol%).
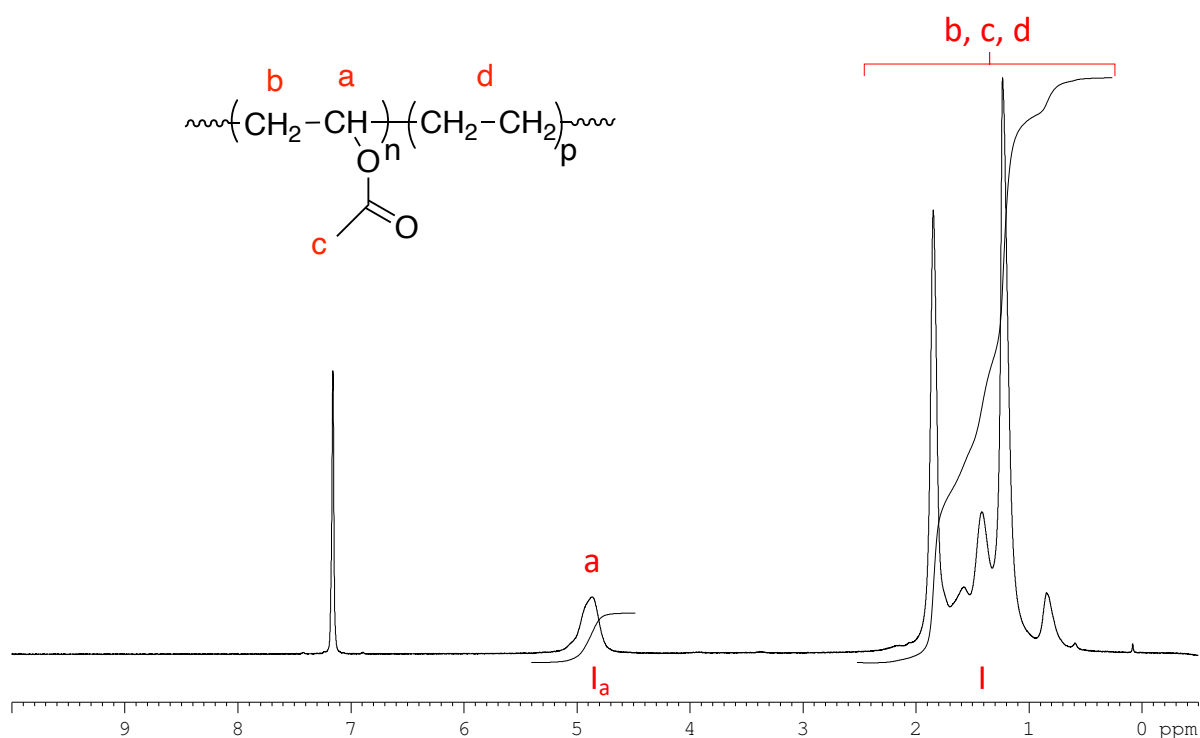

Fig. S6 ^{1}H NMR spectrum of a copolymer of poly(vinyl acetate-*co*-ethylene) L4 in Table 1.

- ***Determination of copolymer compositions by TGA.***

TGA thermograms of P(VAc-*co*-E) copolymers show a typical bimodal decomposition profile (Fig. S7).
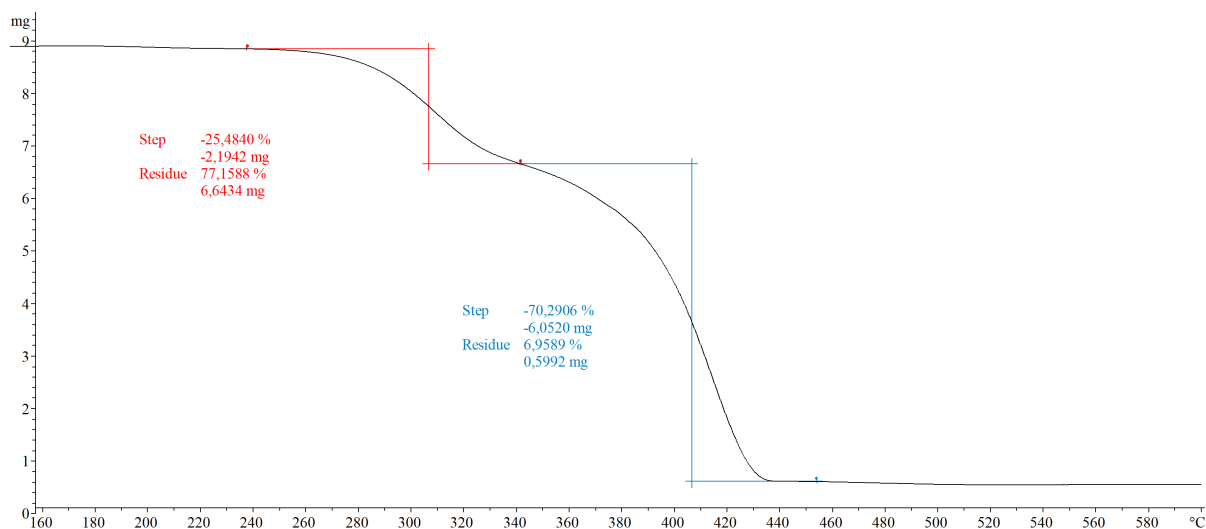

Fig. S7 Thermogram of a copolymer of poly(vinyl acetate-*co*-ethylene) (L11)

The first decomposition stage (250 °C - 350 °C) corresponds to the acetic acid released, whereas the second one is related to the main chain degradation (350 °C – 450 °C). As reported by Gupta,[2] the method can be easily used for elucidating the chemical composition of P(VAc-*co*-E) copolymers.

The total amount of acetic acid produced upon degradation is directly proportional to the VAc content according to Moresco[3] and can thus be used to quantify the VAc content:

$$VAc\ (wt\%) = (\frac{WL \times M_{VAc}}{M_{acetic\ acid}}) \times 100$$

With WL = weight loss of acetic acid (g), M_{VAc} molar mass of vinyl acetate (g mol^{-1}), $M_{acetic\ acid}$ molar mass of acetic acid (g mol^{-1}).

3. References

[1] Rubber, 3. Synthetic–EVM and Ethylene copolymers" Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition, Vol. 31, Wiley VCH Ed., Weinheim, pp 519-523.

[2] Gupta, N.; Srivastava, R. K.; Choudhary, V.; Varma, I. K.; Patnaik, S. *Thermal Characterization of Vinyl Acetate—Ethylene Copolymers.* J. Therm. Anal. Cal. **1999**, *58*, 509-515.

[3] Paradinha, M. M.; Gonzalez Dias, F. T.; Wanke, C. H.; de Lima Novello, J. C.; Tondo, E. C.; De Nardi Martins, J., Bianchi, O. *Preparation and characterization of the ethylene-vinyl acetate copolymer partially hydrolyzed assisted by microwave radiation*. J. Appl. Polym. Sci. **2017,** *134*.