Electronic Supplementary Material (ESI) for Polymer Chemistry.

## Supporting Information

# Nitroxide mediated radical polymerization for the preparation of poly(vinyl chloride) grafted poly(acrylate) copolymers

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## Experimental Procedures

***1/ Chemical compounds:*** PVC was provided by Aldrich ($M_n$ = 43000 g/mol, $M_w$ = 22000 g/mol). The chemicals: $NaN_3$, ethylenediamine tetraacetic acid (EDTA), copper bromide, bipyridine, propargyl acrylate, butyl acrylate (BA), BlocBuilder™ MAMA SG1, DMF, pentane, MeOH, EtOH, acetone, THF, acetone, dichloromethane, $CDCl_3$, DMSO-D6 were purchased from commercial sources (Aldrich, Acros, ABCR or TCI) and used without further purification.

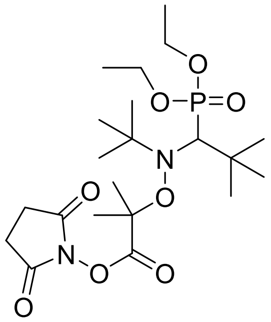
***2/ NMR measurements*****:** NMR spectra were recorded on BRUKER Avance III nanobay – 300 or 400 spectrometers ($^1$H-NMR frequencies 300.13 or 400.13 MHz, respectively, and $^{13}$C-NMR frequencies 75.46 or 100.60 MHz respectively) at 300 K.

***3/ Elemental analysis*****:** CHN elemental analyses were performed at Spectropole Marseille (Aix Marseille University) using a Flash EA analyser, 1112 series Thermo Finnigan driven by the Eager 300 software (oven temperature: 970 °C, gas: helium, flow rate: 140 mL/min, detector: catharometer).

***4/ Mass spectrometry*****:** High resolution mass spectrometry (electrospray ESI-MS) were recorded at Spectropole Marseille (Aix Marseille University) on *a SYNAPT G2 HDMS (Waters) spectrometer equipped with atmospheric pressure ionization source (API). Samples were analyzed in ESI-MS pos*itive mode: electrospray tension: 2.8 kV; exit tension: 20 V; nitrogen nebulization flow: 100 L/h.

***5/ DMA experiment:*** *Dynamic Mechanical Analysis were performed at Westlake Catalyse on a* PerkinElmer DMA 8000 apparatus. Method used: -100 – 150 °C, 3 °C/min, torsion mode, 1 Hz.

Synthesis of MAMA SG1-NHS[1]

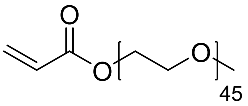


**2,5-dioxopyrrolidin-1-yl2-((tert-butyl(1-(diethoxyphosphoryl)-2,2-dimethylpropyl)amino)oxy)-2-methylpropanoate (MAMA SG1-NHS)**

In a 100 mL two-necked flask, were introduced MAMA SG1 (10.4 mmol, 1 equiv., 4.00 g) and N-Hydroxysuccinimide (11.7 mmol, 1.1 equiv., 1.35 g), dissolved in 10 mL de THF. The mixture was cold to 0 °C and degassed under argon. N,N'-dicyclohexylcarbodiimide (13.5 mmol, 1.3 equiv., 2.8 g) was dissolved in 6 mL of THF and added dropwise at 0 °C. After 3 h, the mixture was filtered and placed at -15 °C overnight and filtered again. Addition of pentane led to the precipitation of **MAMA SG1-NHS**. The solid was filtered, dried under reduced pressure (m = 2.04 g, yield = 41%).

$^1$H RMN (400 MHz, $CDCl_3$) δ: 4.26 (m, 2H, $CH_2$), 4.01 (m, 2H, $CH_2$), 3.31 (d, $J$ = 26.0 Hz, 1H, $CH$-P), 2.83 (s, 4H, $CH_2$-$CH_2$), 1.89 (s, 3H, $CH_3$), 1.82 (s, 3H, $CH_3$), 1.28 (m, 6H, $CH_3$-$CH_2$), 1.21 (s, 9 H, $CH_3$), 1.16 (s, 9H, $CH_3$).

Synthesis of PEG-2000 acrylate **PEGA**[2]



In a 250 mL round botton flask under argon at 0 °C were introduced monoethylether-PEG 2000 (4.96 mmol, 1 equiv., 10 g) in 130 mL of THF and $NEt_3$ (14.9 mmol, 3 equiv., 2.1 mL). Acryloyl chloride (14.88 mmol, 3 equiv., 1.21 mL) was dissolved in 20 mL of THF and then added dropwise into the reaction mixture at 0 °C. The white solution turned to yellow after few hours. After reaction, the reaction mixture was filtered, and all volatiles were removed under reduced pressure. The resulting solid was dissolved in the minimum volume of $CHCl_3$ and then precipitated with a mixture of diethyl ether and ethanol (90:10) at 0 °C. The mixture was placed in the freezer (-15 °C) for 2 h, then filtered and washed with cold diethyl ether. (m = 7.8 g, r = 69%, $M_n$ = 2700 g/mol, Đ = 1.05)

$^1$H RMN (400 MHz, $CDCl_3$) δ: 6,42 (d, J=17,3 Hz, 1H, C=CH$H$), 6,15 (m, 1H, $CH_2$=C$H$), 5,83 (d, J=10,4 Hz, 1H, C=C$H$H), 4,31 (m, 2H, O-$CH_2$), 3,64 (m, 180H, O-$CH_2$-$CH_2$-O), 3,37 (s, 3H, $CH_3$).

Molecular weight of PEGA (SEC-THF using PS standard) : $M_n$ = 2700 g/mol, Đ = 1.05.

DSC of PEGA: $T_m$ = 52.9 °C.

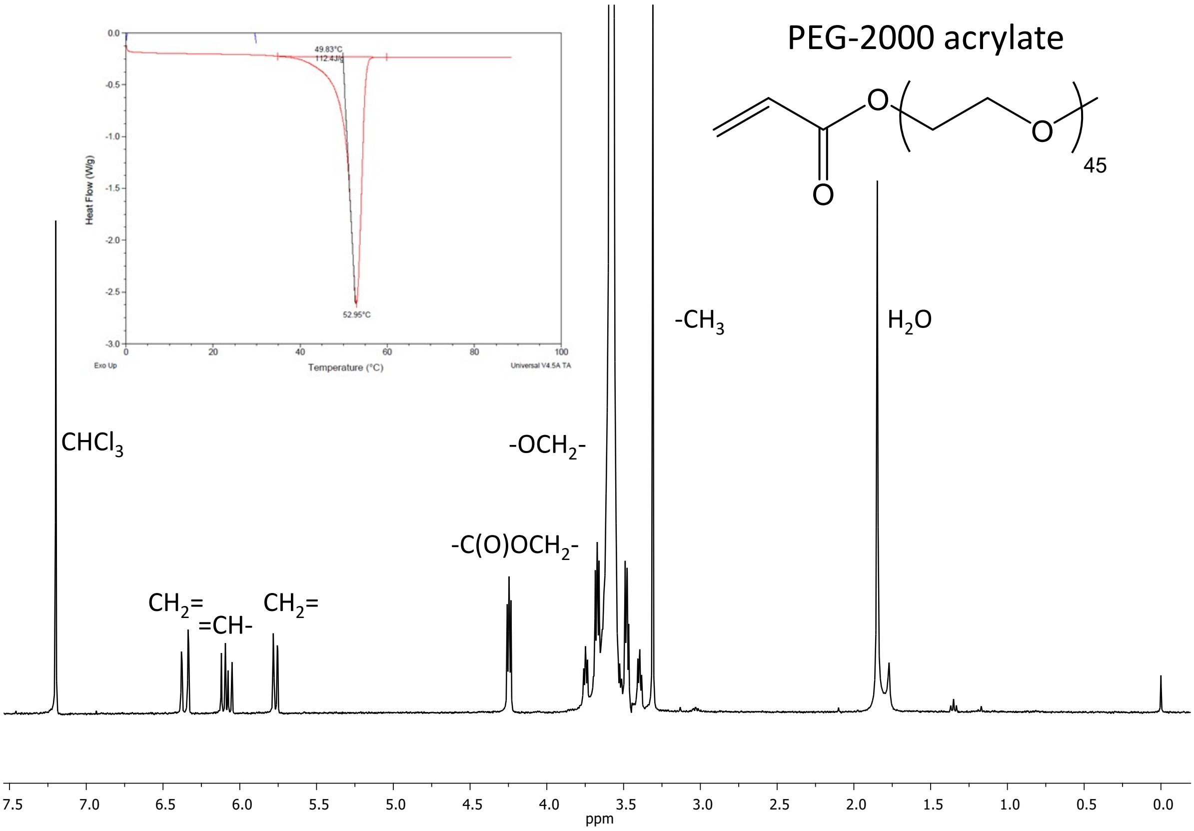


**Figure S1. $^1$H NMR and DSC thermogram of PEGA**

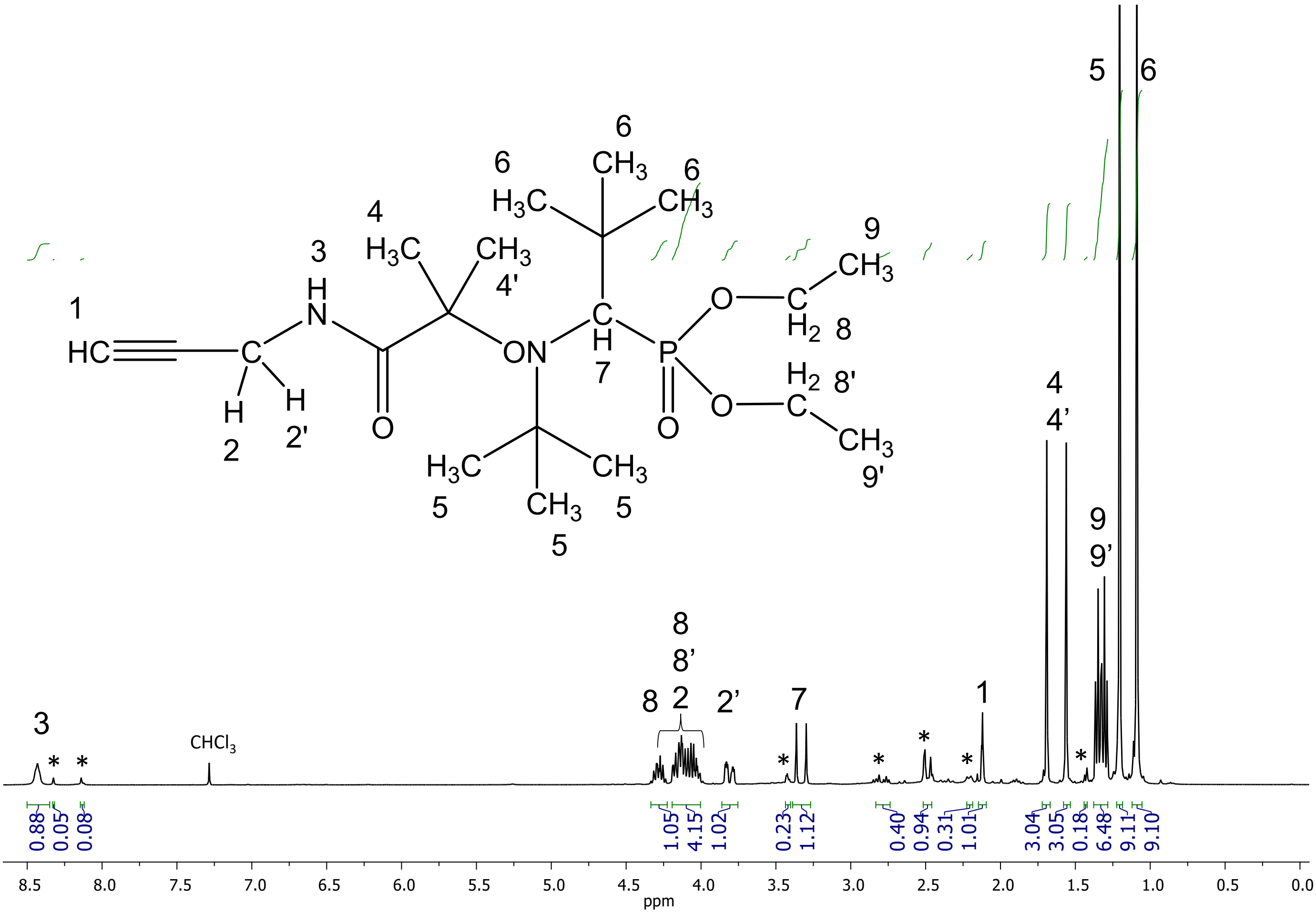


**Figure S2. $^1$H NMR of alkoxyamine 1 (unidentified impurities marked with *).**

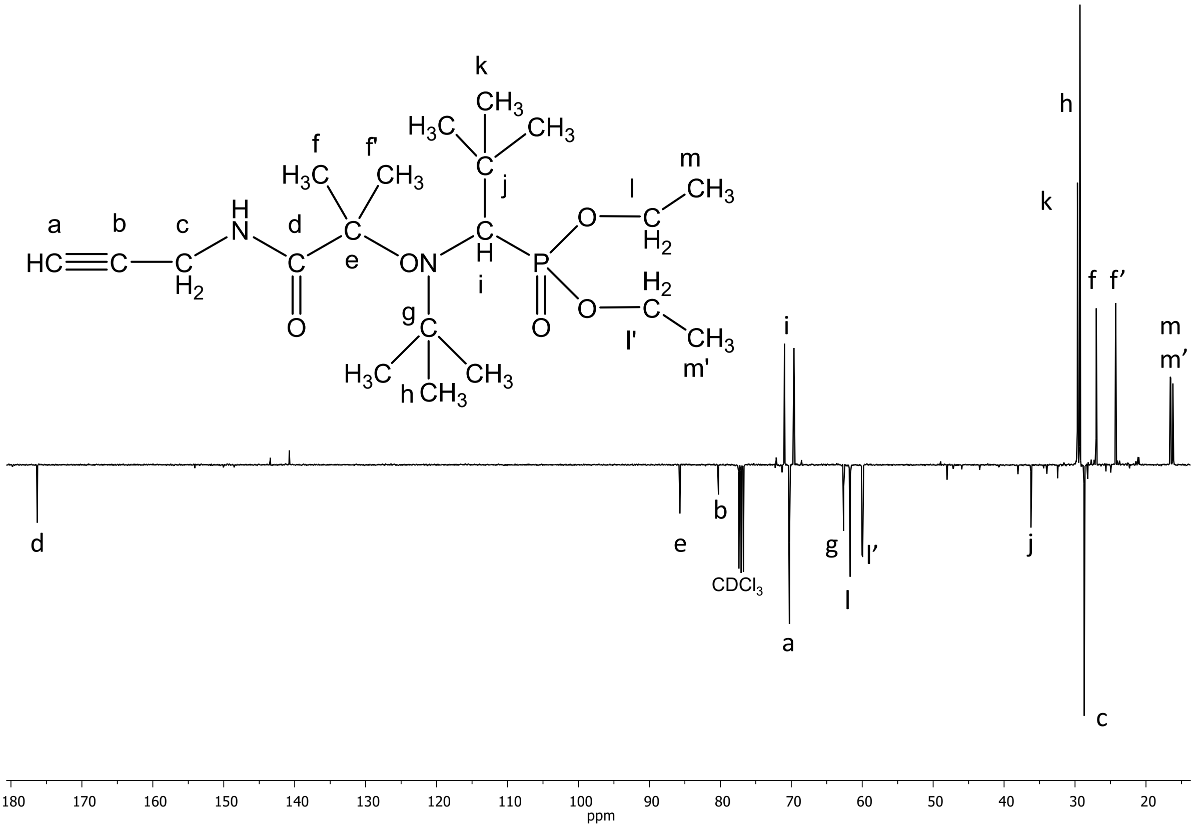


Figure S3. $^{13}$C-APT NMR of alkoxyamine 1 Alk1

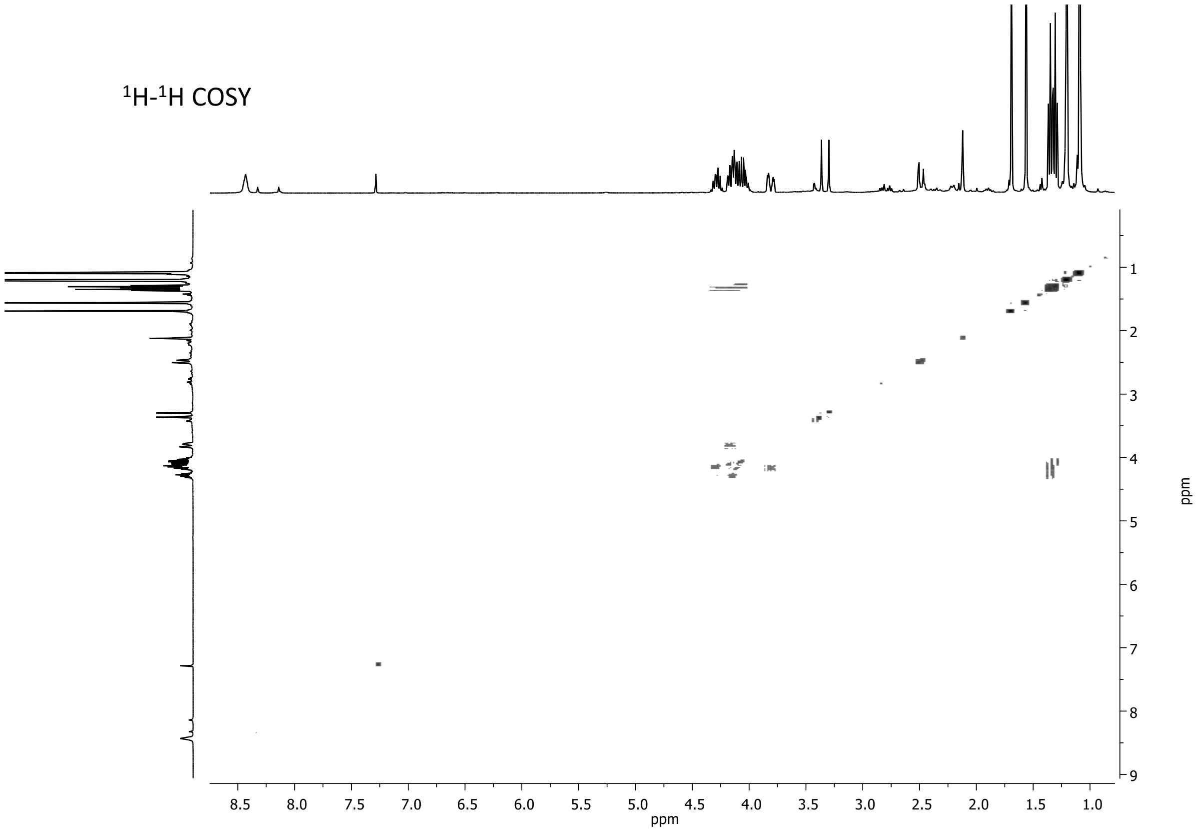


Figure S4. Correlation spectroscopy $^1$H-$^1$H COSY NMR of alkoxyamine 1 Alk1

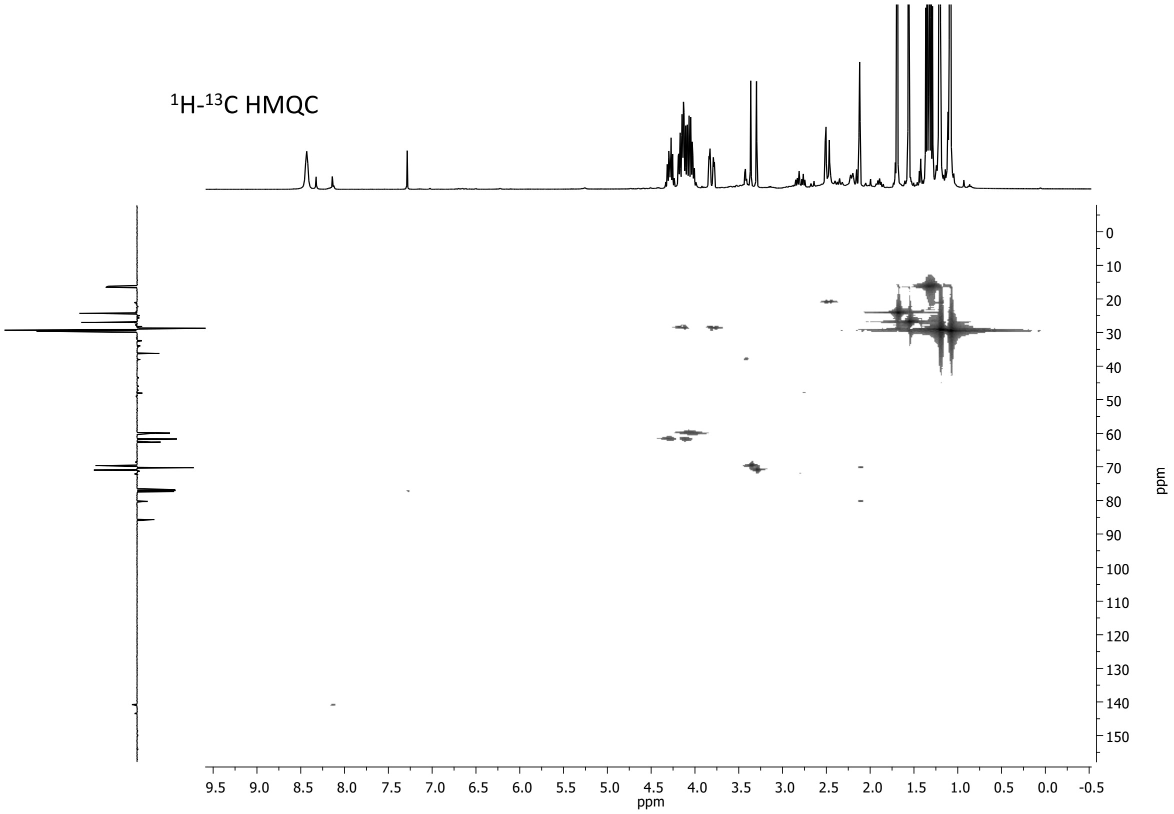


**Figure S5. Heteronuclear Multiple-Quantum Correlation HMQC NMR of alkoxyamine 1 Alk1**

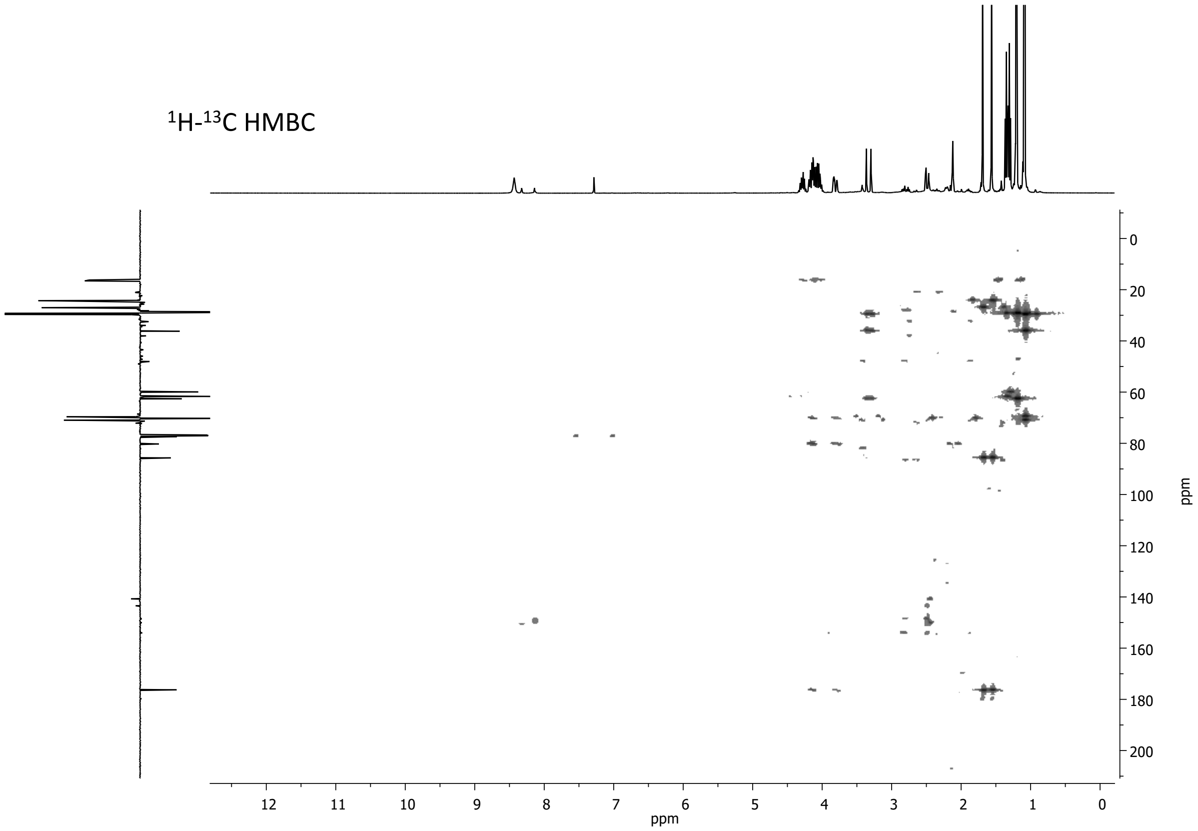


**Figure S6. Heteronuclear Multiple Bond Correlation HMBC NMR of alkoxyamine 1 Alk1**

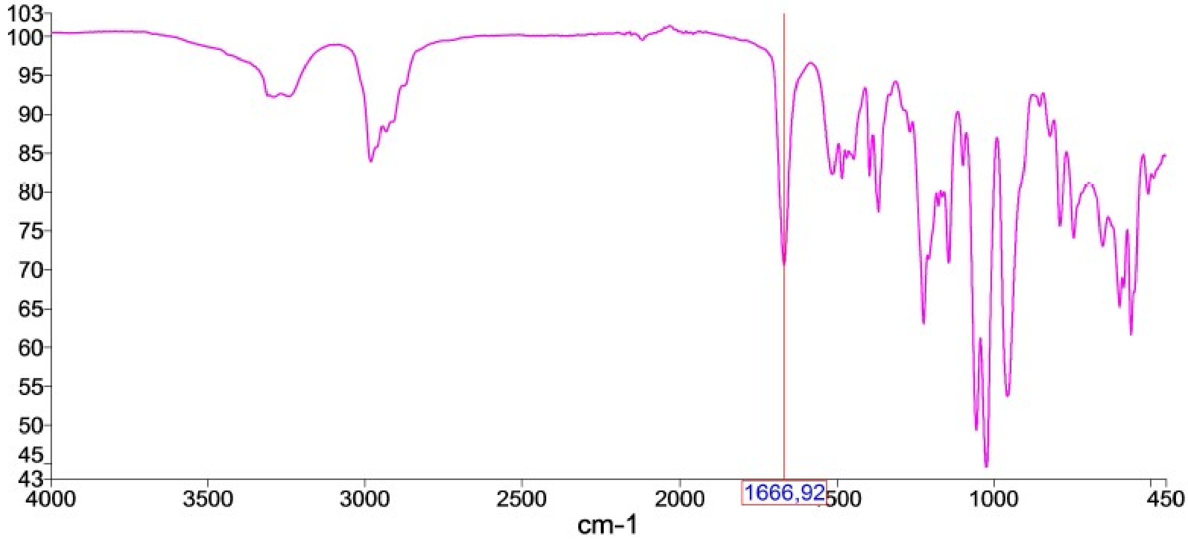


**Figure S7. ATR-IR spectrum of alkoxyamine 1 Alk1**

### Bond dissociation energy measurement of alkoxyamine 2.

The evolution time of the doubly integrated ESR signal of the nitroxide radicals was followed by ESR spectroscopy. The appearance of the nitroxides in a temperature range (80 °C) was then monitored in *tert*-butyl benzene (0.5 mL) containing initially typically $10^{-4}$ M solution of alkoxyamines. $O_2$ was used as a radical scavenger. Samples with known concentrations of the persistent nitroxide radicals were used as calibration standards. Bond dissociation energy for the C-O homolysis: calculated to 117 kJ/mol.[3]

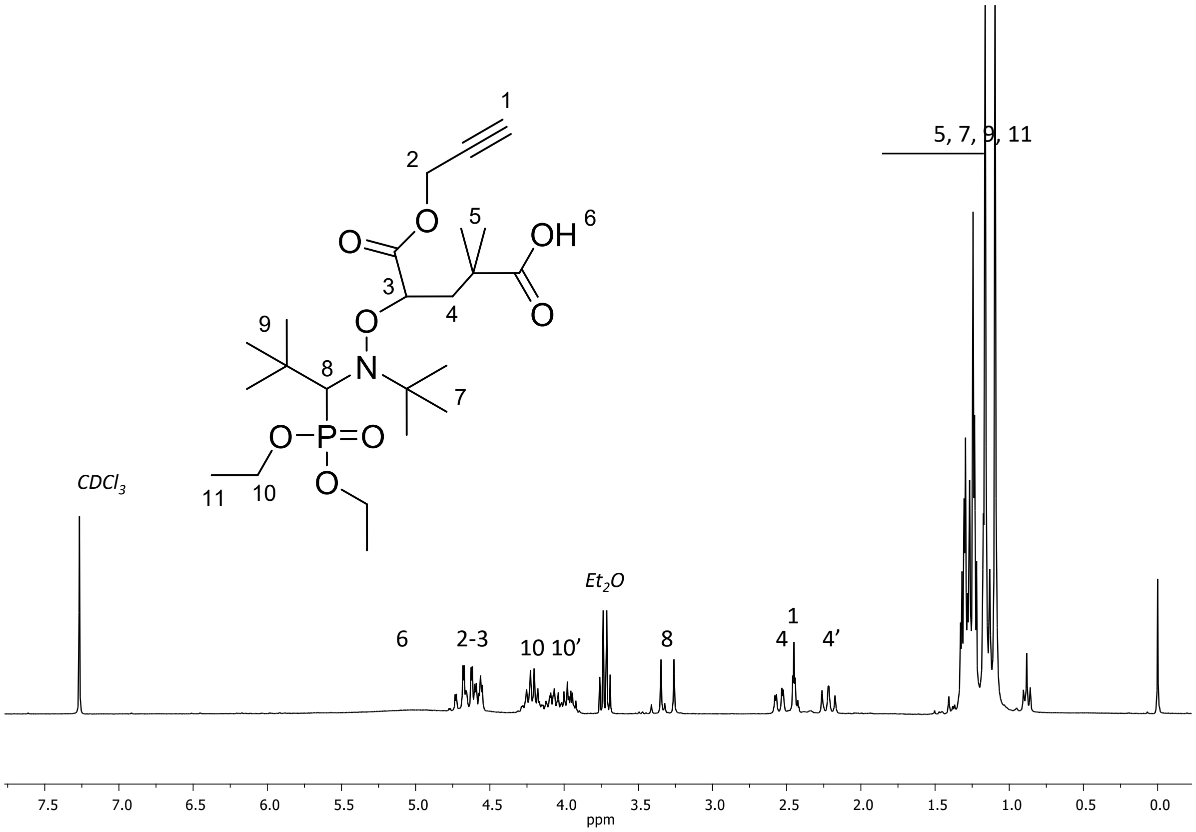


**Figure S8. $^1$H NMR of alkoxyamine 2.**

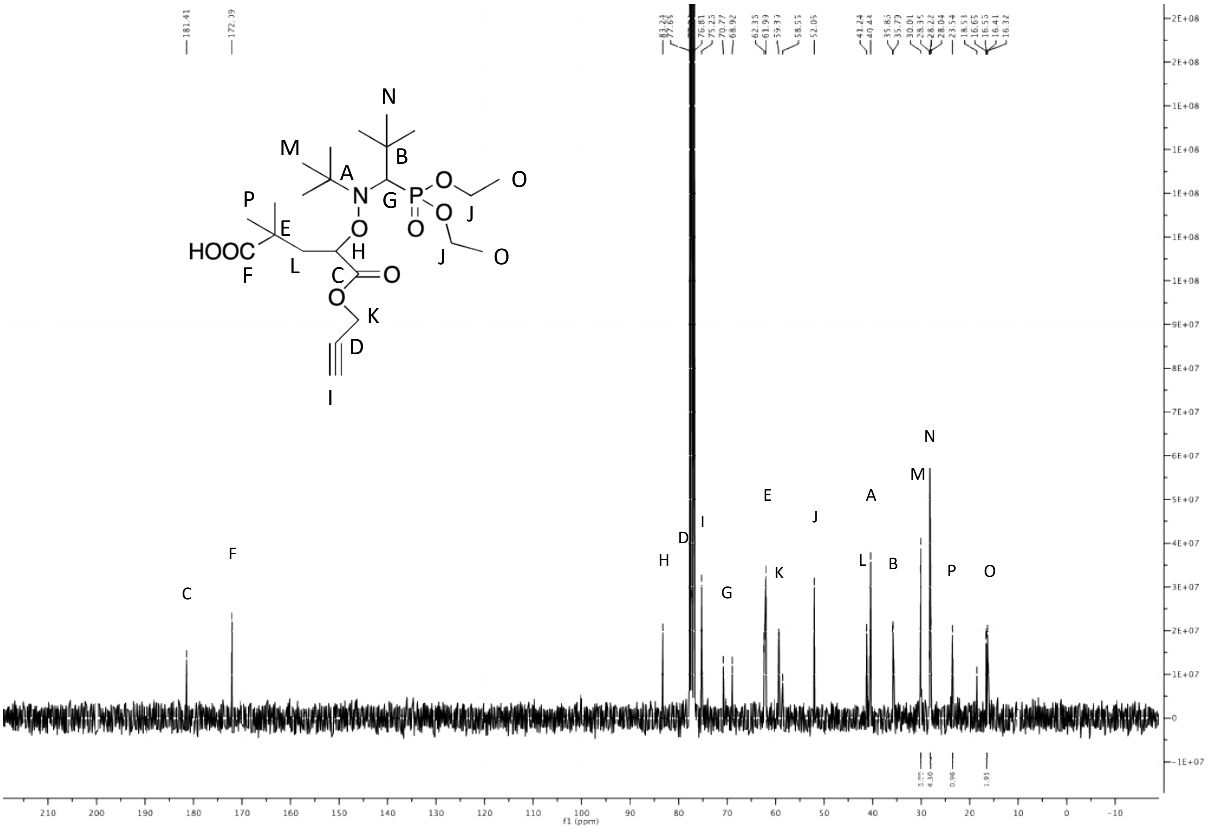


**Figure S9. $^{13}$C NMR of alkoxyamine 2.**

## 2.3. Preparation of azide functional PVC (PVC-$N_3$)

Typical procedure for PVC-$N_3$ preparation: in a 250 mL round bottom flask, PVC (4 g) and $NaN_3$ (4 g) were introduced in 70 mL of DMF. The mixture was heated at 60 or 50 °C for 1 to 16.5 h (see Table S1). The mixture was filtered and then precipitated via a dropwise addition of the solution onto 400 mL of ethanol under high magnetic stirring. After filtration, the solid was dissolved in 100 mL of THF and precipitated in 400 mL of ethanol. The solid was dried under reduced pressure.

$^1$H RMN (400 MHz, $CDCl_3$) δ: 4.59 - 4.16 (br m, 1H, CH), 2.42 – 1.88 (br m, 2H, $CH_2$).

IR (cm$^{-1}$): 2910, 2108, 1426, 1331, 1254, 1098, 962, 655, 611.

The concentrations of grafted azide were determined by elemental analysis using the N% (see Table 1).

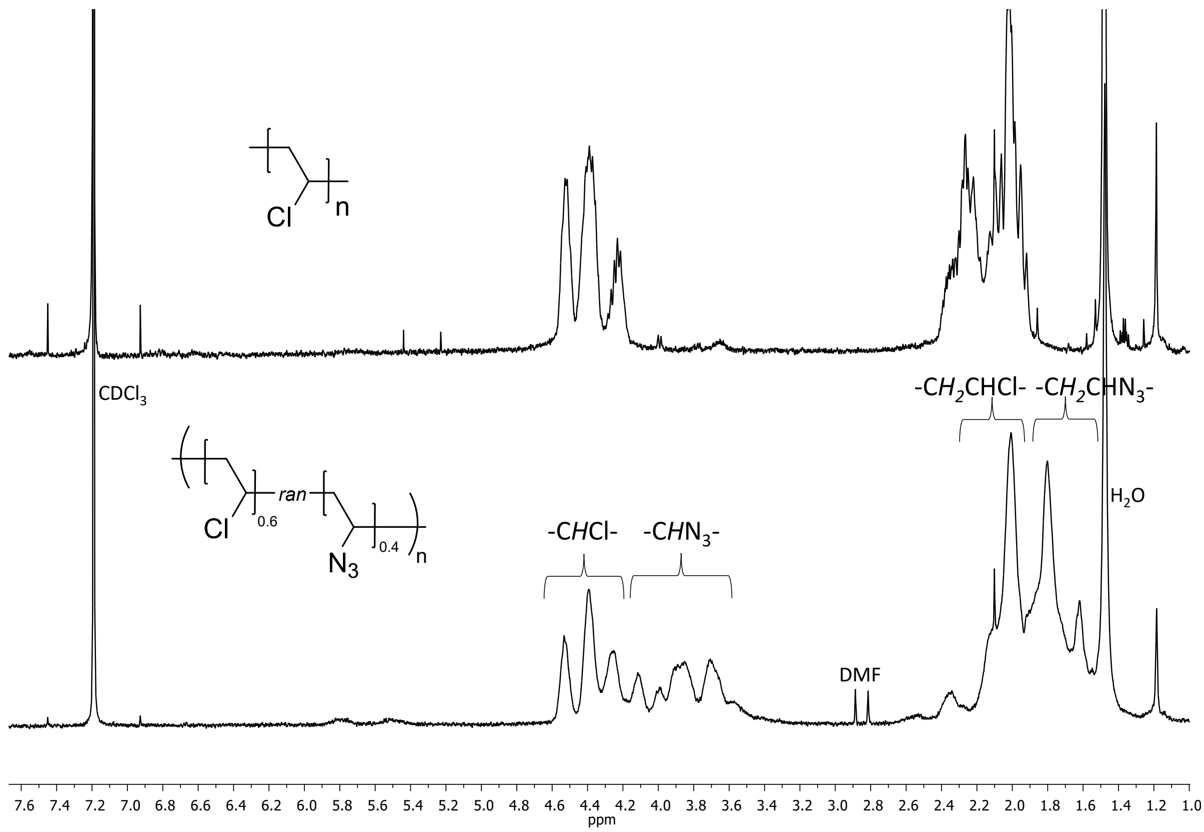


**Figure S10. $^1H$ NMR spectra of PVC and PVC-$N_3$ (containing 43% of azide units)**

**Table S1.** PVC-$N_3$ analysis.

| entry | Reaction time (h) | Temp. (°C) | C wt% | H wt% | N wt% | % units $N_3$ |
|---|---|---|---|---|---|---|
| 1 | 1 | 60 | 38.36 | - | 2.98 | 4.4 |
| 2 | 1 | 60 | 38.56 | 4.79 | 3.13 | 4.7 |
| 3 | 2.75 | 60 | 39.56 | - | 11.73 | 18 |
| 4 | 4 | 60 | 38.65 | - | 17.64 | 27 |
| 5 | 5.5 | 60 | 38.04 | - | 24.62 | 38 |
| 6 | 8.25 | 60 | 39.19 | - | 20.75 | 32 |
| 7 | 11 | 60 | 38.35 | - | 28.22 | 43 |
| 8 | 16.5 | 60 | 37.85 | 4.82 | 21.65 | 33 |
| 9 | 0.33 | 50 | - | - | 0.96 | 1.4 |
| 10 | 1 | 50 | - | - | 2.98 | 3.4 |

Calculation of % of $N_3$-modified unit of from elemental analysis:

$$wnt\%\ of\ N = \frac{(14*3)*x}{62.5*(1-x)+69*x} \quad \text{Equation 1}$$

where x = % of $N_3$-modified units, M of PVC units ($CH_2$-CHCl) = 62.5 g/mol and M of $N_3$-modified units ($CH_2$-$CHN_3$) = 69 g/mol

From equation 1, we determined x (% of $N_3$-modified units):

$$x = \frac{Wt\%\ of\ N*62.5}{(Wt\%\ of\ N*62.5)+14*3-(Wt\%\ of\ N*69)} \quad \text{Equation 2}$$

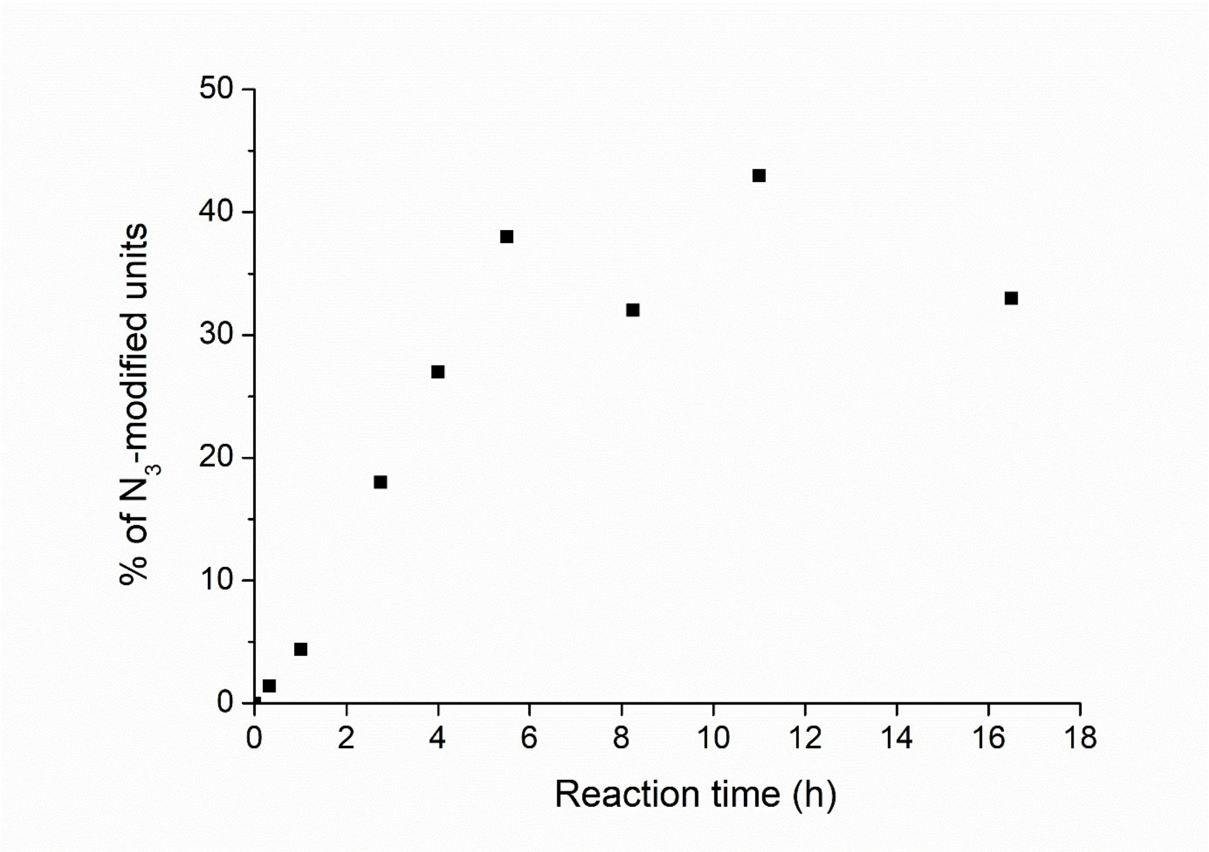


**Figure S11. Conversion of –($CH_2CHCl$)- units into –($CH_2CHN_3$)- in PVC with reaction time.**

### Synthesis of PVC-Alk1

In a 100 mL round bottom flask, 100 mg of PVC-$N_3$ (containing 4.4% of azide-modified units) were dissolved in 6 mL of DMF and then 34 mg of alkoxyamine 1 were added. Under argon, CuBr (11 mg, 0.08 mmol), and bipyridine (28 mg, 0.017 mmol) were added and the reaction was performed for 18 h at 30 °C under argon. PVC-Alk1 was precipitated with 200 mL of water and the resulting solid was washed with 100 mL of ethanol. The solid was dried under reduced pressure. The solid was not soluble in DMSO-$D_6$ but the IR spectrum showed the presence of alkoxyamine 1 and some residual azide functions (Figure S12).

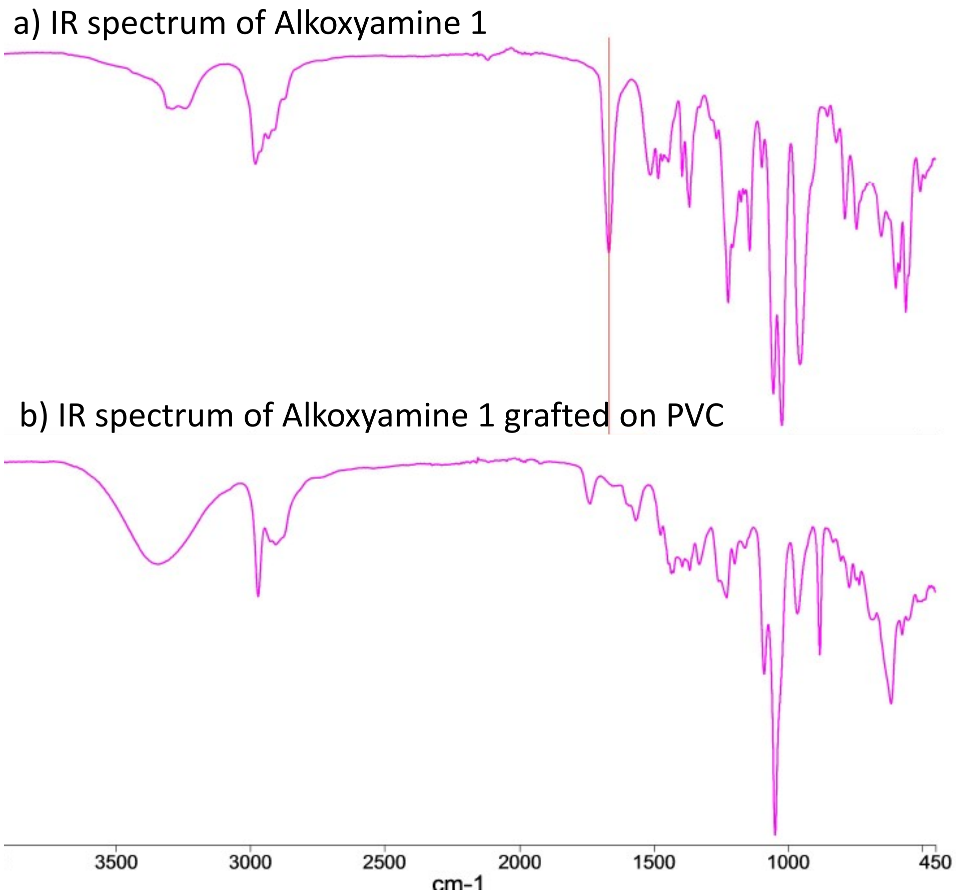


**Figure S12. Comparison of IR spectrum of alkoxyamine 1 and the solid resulting from the CuAAC reaction of PVC-$N_3$ and alkoxyamine 1.**

### Synthesis of PVC-Alk2

The synthesis of PVC-Alk2 was performed from PVC-$N_3$ containing 4.7% of $N_3$-modified units and PVC-$N_3$ containing 1.4% of $N_3$-modified units. Analysis of the PVC-Alk2 is presented in Table S2. SEC analysis of PVC-Alk2 using PS cal. : $M_n$ = 16800 g/mol, $M_w$ = 65100 g/mol, Đ = 3.9.

**Table S2.** $^1$H NMR and elemental analysis of PVC-Alk2

| $N_3$ units in PVC-$N_3$ | CH $^1$H NMR integral (4.7-4.2 ppm) | $CH_3$ $^1$H NMR integral (1.4-1.0 ppm) | mol% of Alk2 according to NMR | Elemental analysis Oxygen (wt%) | mol% of Alk2 according to O% |
|---|---|---|---|---|---|
| 4.7% | 1.00 | 1.14 | 3.8% | 6.25 | 4.0% |
| 1.4% | 1.00 | 0.44 | 1.5% | 2.50 | 1.4% |

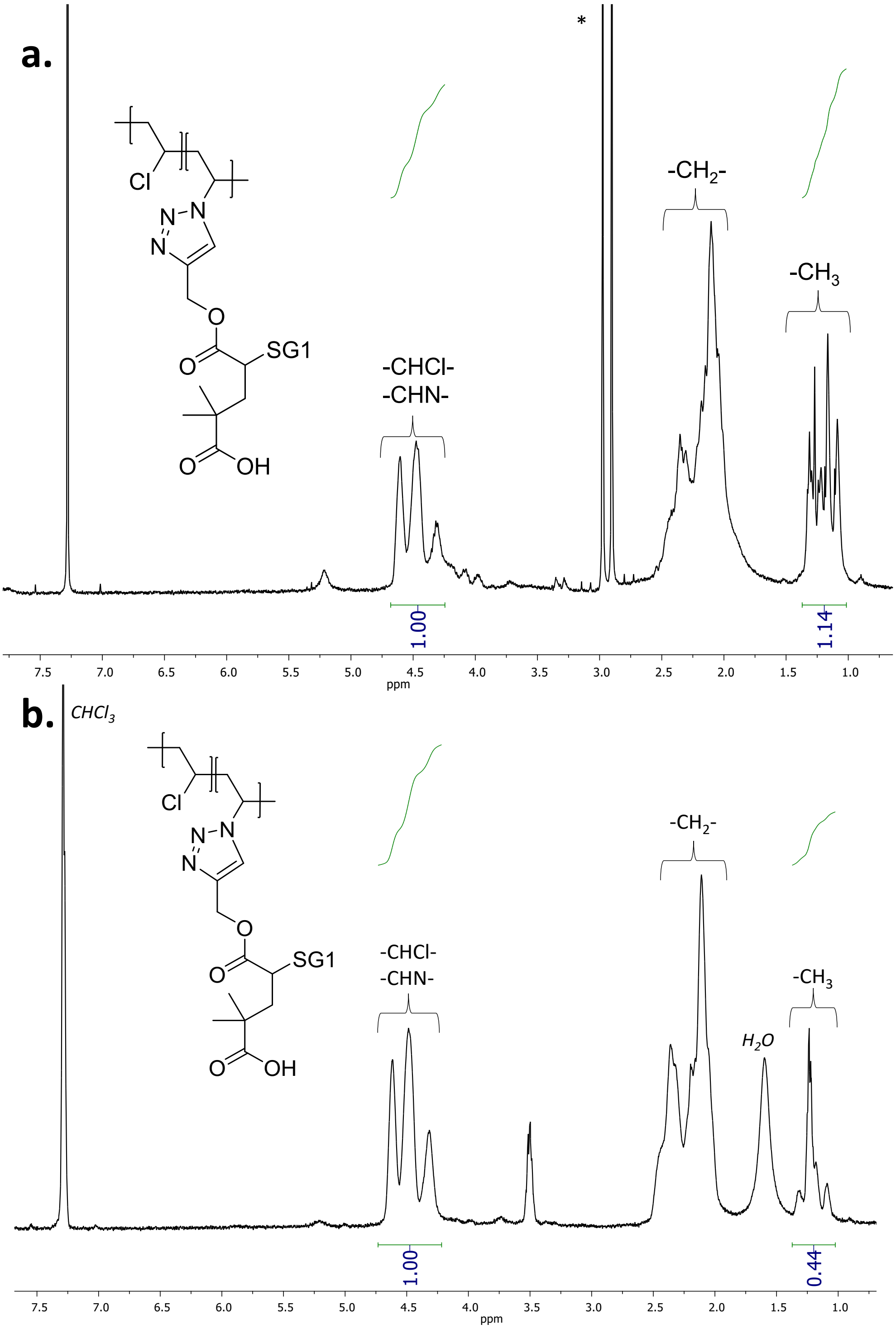


**Figure S13. $^1$H NMR spectra of PVC-Alk2 (a. prepared from PVC-N3$_{4.7\%}$, b. prepared from PVC-N3$_{1.4\%}$, Table S2).**

## Polymerization of butyl acrylate (BA) with alkoxyamine 2

Alkoxyamine 2 (63 mg, 0.138 mmol), BA (2 mL, 13.88 mmol) and 4 mL of DMF were mixed under argon in a Schlenk flask. The mixture was heated at 100 °C and aliquots of the solution were taken for $^1$H NMR to evaluate the BA conversion and SEC to determine the molecular weight of the PBA. The results are presented in Table S3.

**Table S3.** BA polymerization initiated by alkoxyamine 2

| Time<br>[h] | Conversion<br>[%][a)] | $M_n$<br>[g/mol] [b)] | $M_w$<br>[g/mol] [b)] | *Đ* [b)] | *Mn theo* |
|---|---|---|---|---|---|
| 0,5 | 13 | 3050 | 5180 | 1.70 | 1700 |
| 1 | 17 | 3520 | 5880 | 1.67 | 2200 |
| 2 | 24 | 3920 | 6660 | 1.69 | 3100 |
| 4 | 80 | 8540 | 19000 | 2.22 | 10200 |
| 6 | 85 | 8640 | 19600 | 2.26 | 10900 |

Conditions: 100 °C, BA/DMF ratio of 1/2, BA/alkoxyamine ratio of 100/1. a) Determined by $^1$H NMR; b) determined by SEC in THF using PS calibration

**Table S4.** synthesis of PVC-*g*-PBA

| entry | Mass<br>of Alk2 (g) | Volume<br>of BA (mL) | Time<br>(h) | Conversion of BA[a)] | BA<br>[wt%][b)] | $T_g$<br>[°C][c)] |
|---|---|---|---|---|---|---|
| 1 PVC [d)] | - | - | - | - | - | 82 |
| 2 | 0.20 | 0.5 | 6 | 0.15 | 20 | 63.5 |
| 3) | 0.20 | 0.5 | 6 | 0.11 | 25 | 56 |
| 4 | 0.09 | 0.5 | 6 | 0.11 | 40 | 42 |
| 5 | 0.09 | 0.5 | 6 | 0.15 | 44 | 38 |
| 6 | 0.09 | 0.5 | 9 | 0.22 | 51 | 12.5 |
| 7 | 0.09 | 0.5 | 7 | 0.19 | 53 | 7.5 |
| 8 | 0.09 | 0.5 | 12 | 0.35 | 60 | 4.5 |
| 9 | 0.09 | 0.5 | 9 | 0.24[e] | 66 | 0.5 |
| 1 | 0.09 | 0.5 | 11 | 0.37 | 71 | -1 |
| 11 | 0.09 | 0.5 | -[f] | 0.52 | 88 | -10.5 |

Conditions: 100 °C, BA/DMF ratio of 1/4, BA/alkoxyamine ratio of 67/1, polymerization initiated using PVC-Alk2 synthesized from a PVC-$N_3$ containing 4.7% of azide units. a) Determined by $^1$H NMR from aliquots of the reaction medium; b) Determined by $^1$H NMR after precipitation of copolymer; c) determined by DSC; d) PVC purchased from Aldrich; e) a relative low BA conversion was obtained, compared to the high BA concentration in resulting PVC-*g*-PBA (no explanation); f) not determined.

### Evaluation of BA concentration in PVC-*g*-PBA by $^1$H NMR:

The integrals of -$CH_3$ signals (singlet signal at 1-0.9 ppm) was used as reference. Overlapped signals between 4.7-3.8 ppm are attributed to -CHCl- of PVC units and C(O)O-$CH_2$- of BA units. The molar weight of the azide-Alk2 units was not negligeable (14*3 + 491.6 g/mol) and included in the calculations.

Integrals of -CHCl- of PVC units: I = [(4.7-3.8ppm integral) – 2]

Molar mass of VC: 62.5 g/mol and 4.7% of ($N_3$-Alk2): 0.047 * (14*3 + 491.6) = 25 g/mol

; molar mass of BA: 128 g/mol

$$Wt\%\ of\ BA\ in\ PVCgPBA = \frac{128}{(62.5 + 25) * (I) + 128}$$

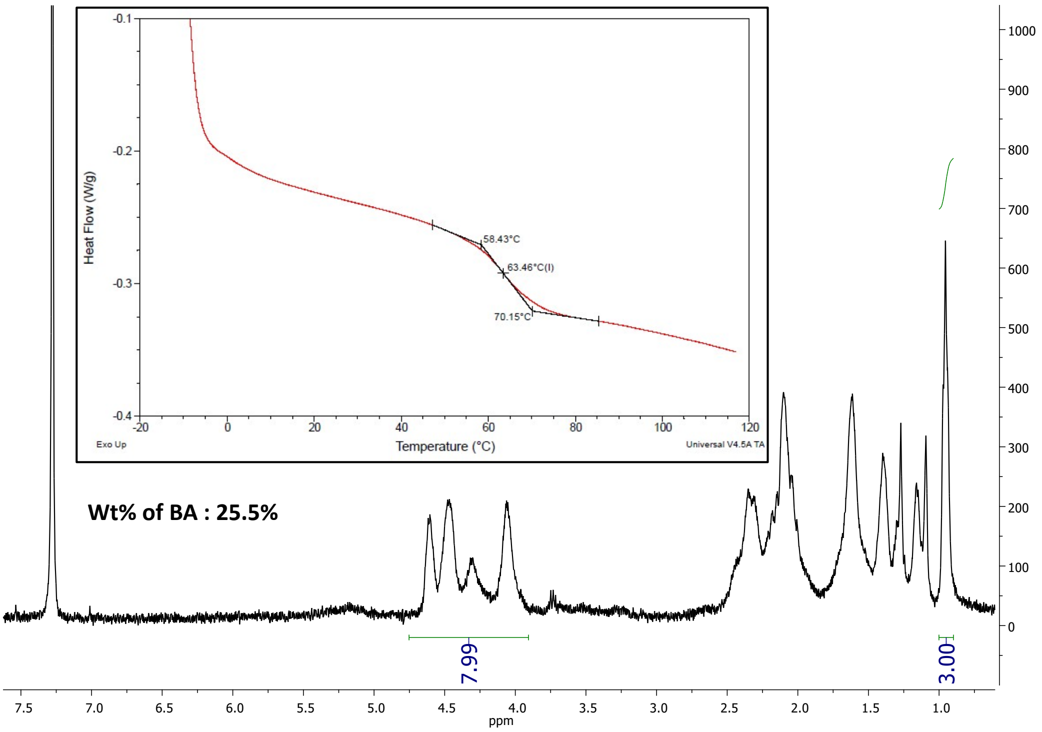


Figure S14a. $^1$H NMR spectrum and DSC thermogram of PVC-g-PBA containing 20 wt% of BA.

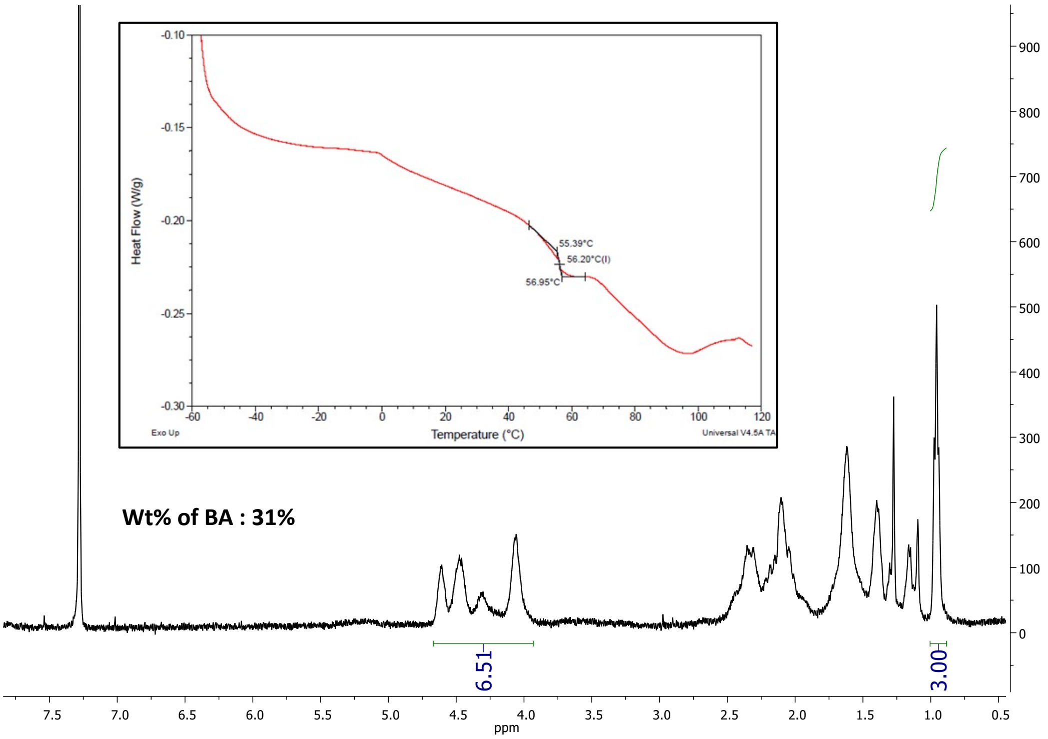


Figure S14b. $^1$H NMR spectrum and DSC thermogram of PVC-g-PBA containing 25 wt% of BA.

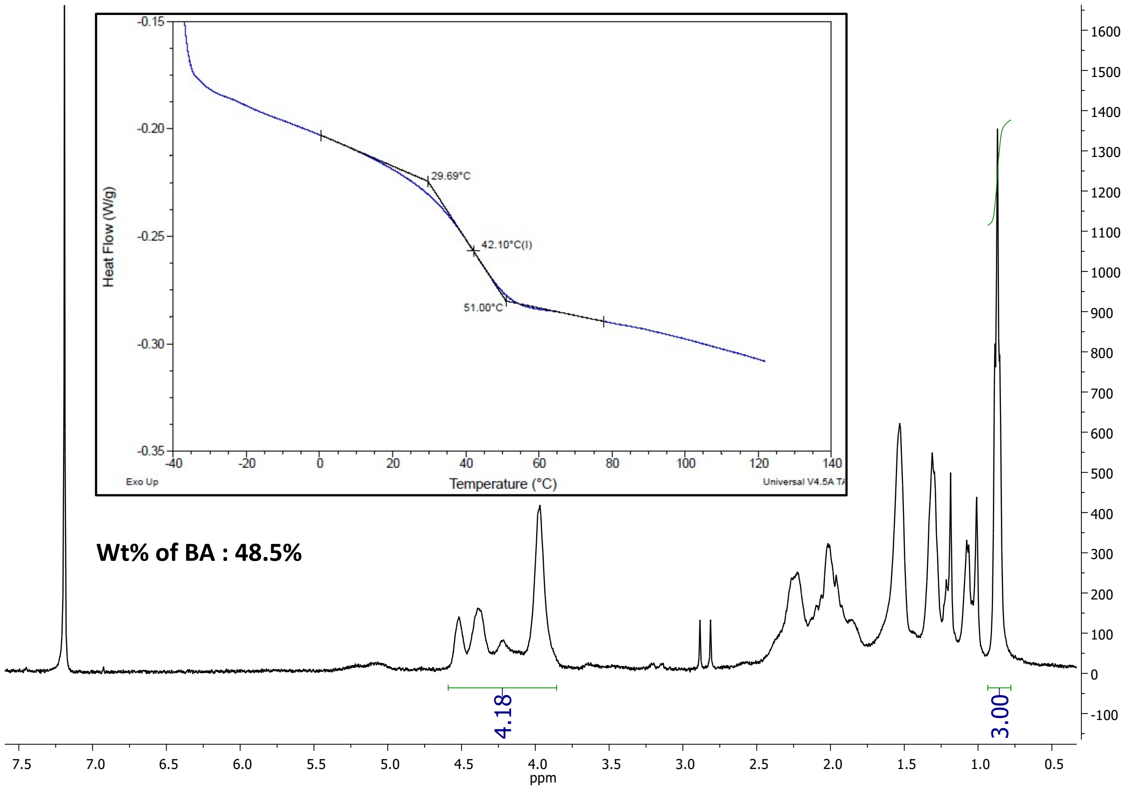


Figure S14c. $^1$H NMR spectrum and DSC thermogram of PVC-g-PBA containing 40 wt% of BA.

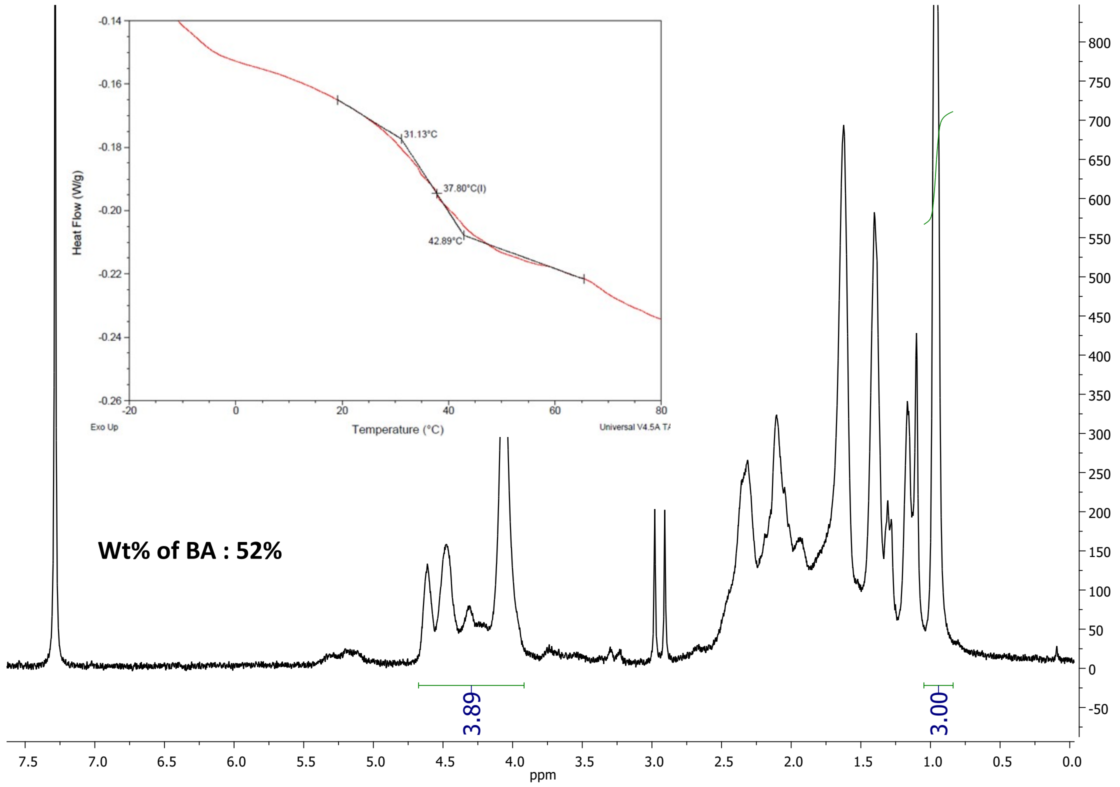


Figure S14d. $^1$H NMR spectrum and DSC thermogram of PVC-g-PBA containing 44 wt% of BA.

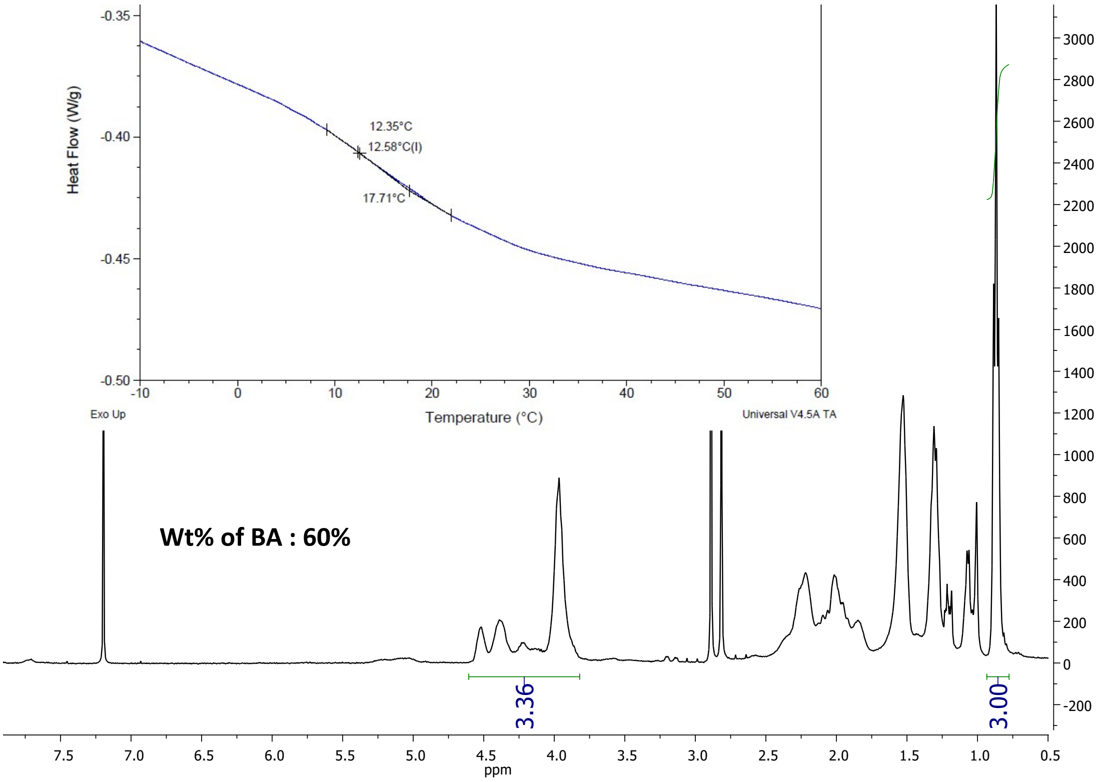


Figure S14e. $^1$H NMR spectrum and DSC thermogram of PVC-g-PBA containing 51 wt% of BA.

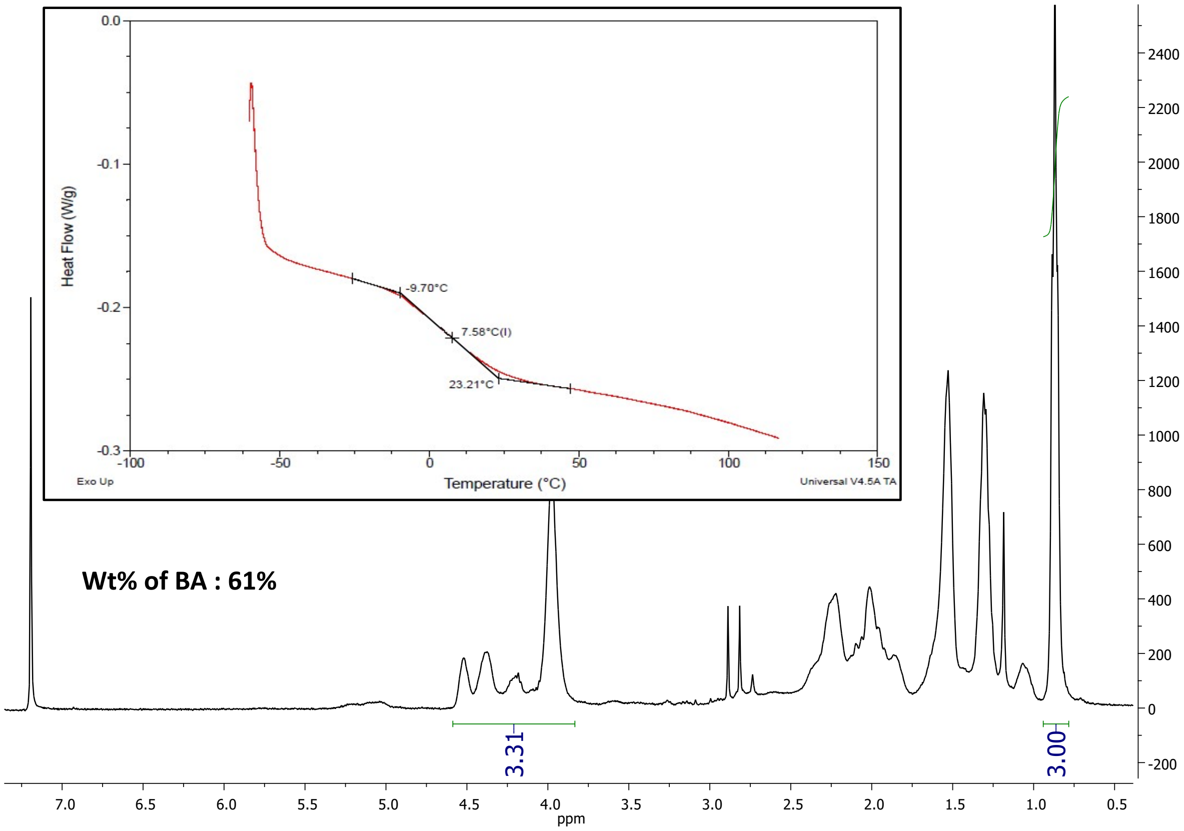


Figure S14f. $^1$H NMR spectrum of DSC and thermogram of PVC-g-PBA containing 53 wt% of BA.

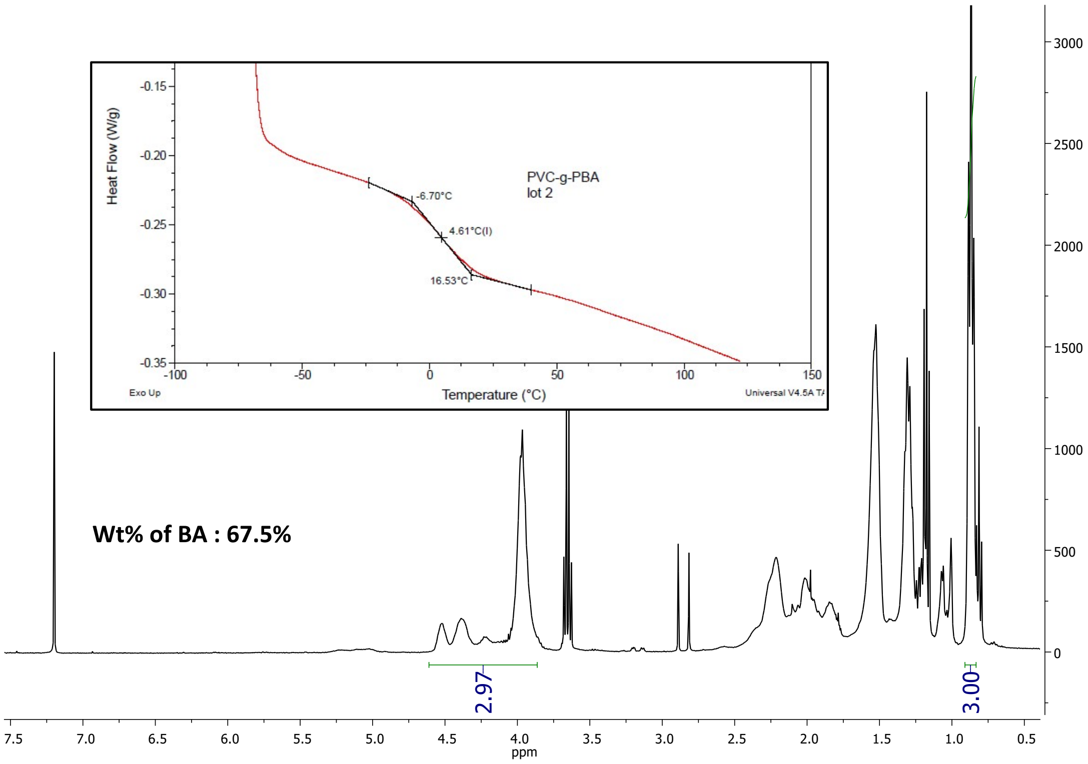


Figure S14g. $^{1}H$ NMR spectrum and DSC thermogram of PVC-g-PBA containing 60 wt% of BA.

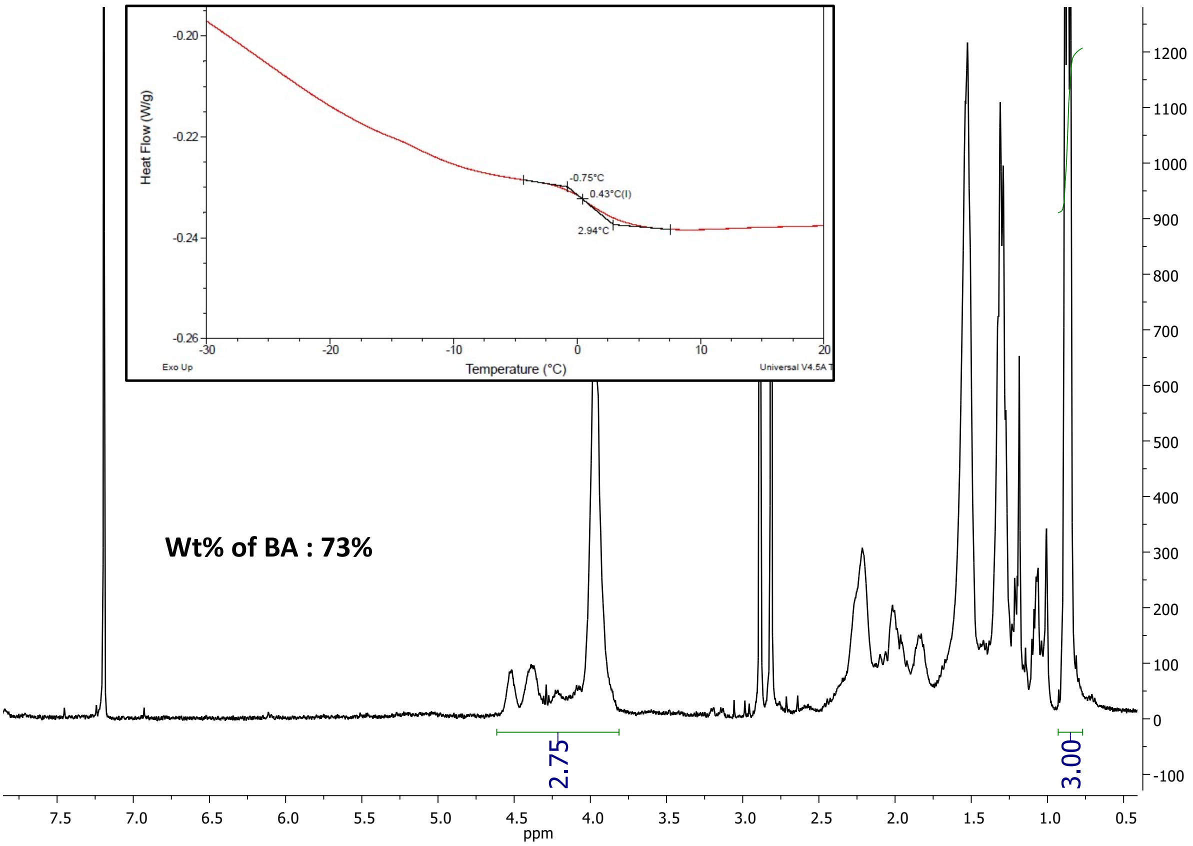


Figure S14h. $^{1}H$ NMR spectrum and DSC thermogram of PVC-g-PBA containing 66 wt% of BA.

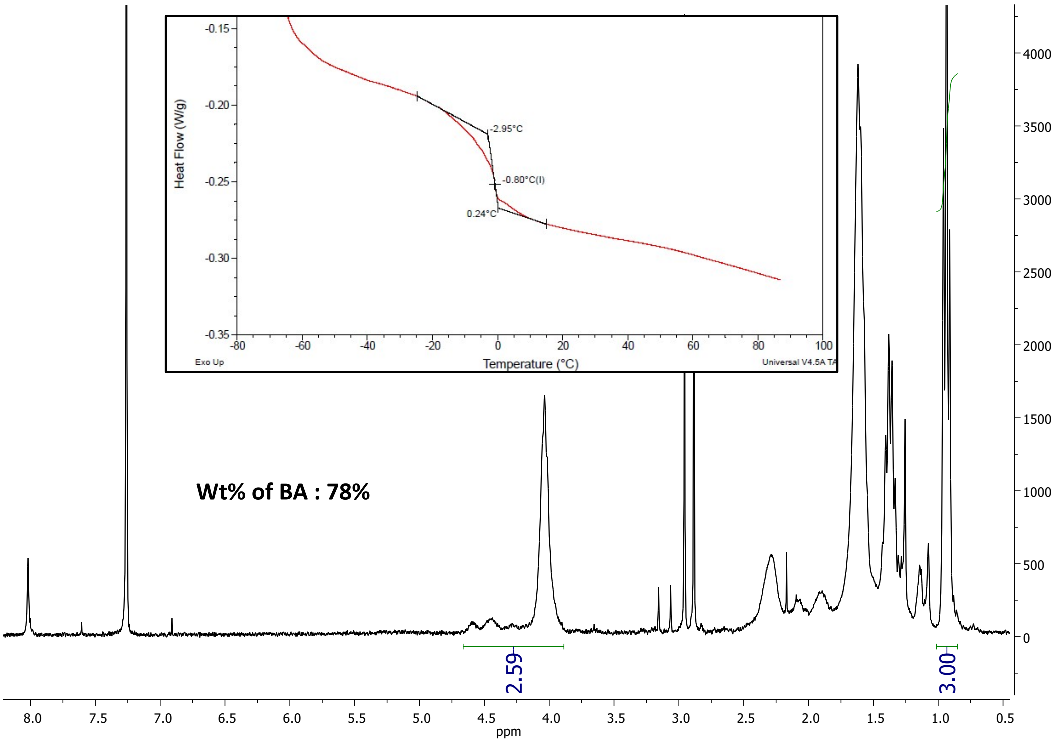


Figure S14i. $^1$H NMR spectrum and DSC thermogram of PVC-g-PBA containing 71 wt% of BA.

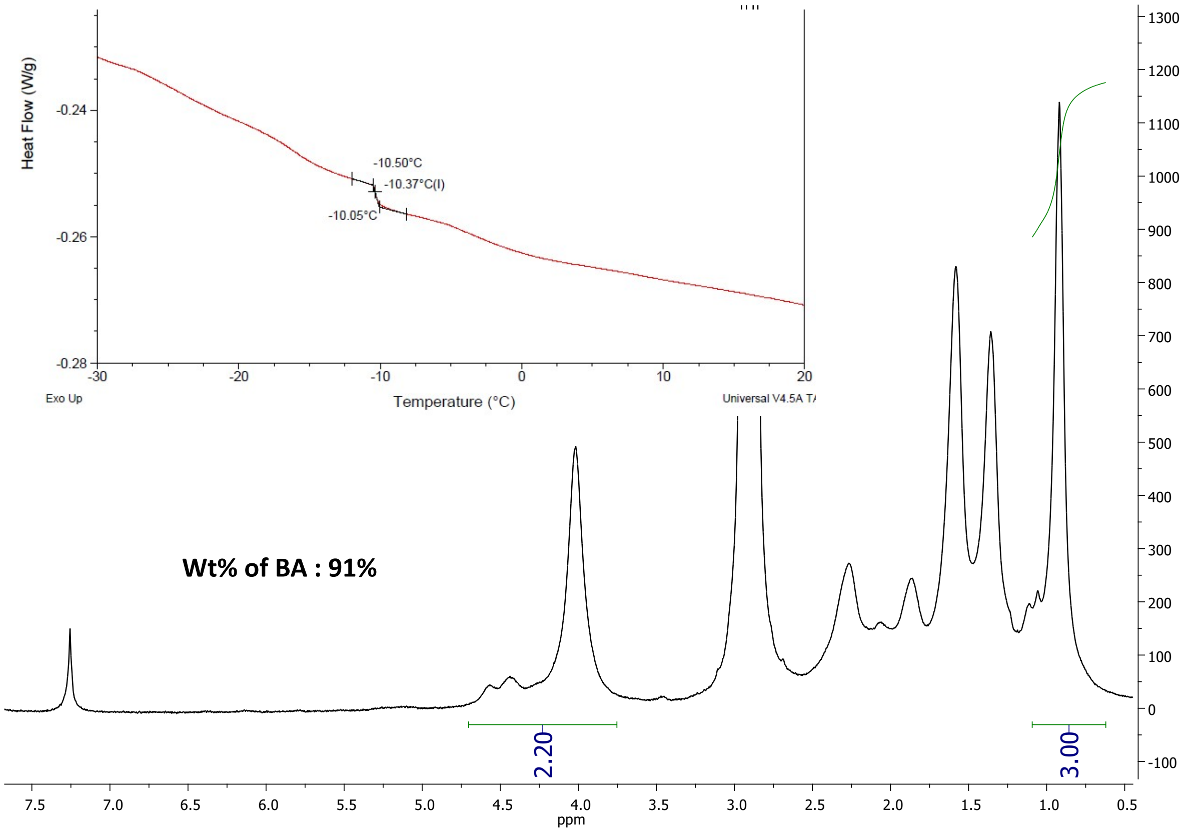


Figure S14j. $^1$H NMR spectrum and DSC thermogram of PVC-g-PBA containing 88 wt% of BA.

### Polymerization of $PEG_{2000}$ acrylate (PEGA) with PVC-Alk2

PVC-*g*-PEGA were prepared using PVC-Alk2 (synthesized from a PVC-N3 containing 1.4% of $N_3$ units) and PEG acrylate (Table S5) dissolved in 15 mL of DMF under argon. The mixtures were heated at 100 °C for 18 h. The PEGA conversions (Table S5) and PEGA concentrations in PVC-*g*-PEGA were evaluated by $^1$H NMR (Figures S15a-c).

**Table S5.** PEG-2000 acrylate (PEGA) polymerization initiated by PVC-Alk2

| Mass of Alk2 | Mass of PEGA | Mass of PVC-g-PEGA | Equiv PEGA | Conv.[a)] |
|---|---|---|---|---|
| 1.85 g | 0.71 g | 1.70 g | 1 equiv | 55% |
| 1.52 g | 1.10 g | 1.95 g | 2 equiv | 46% |
| 1.20 g | 1.60 g | 1.70 g | 4 equiv | 61% |

Conditions: 100 °C, DMF, 18 h, the polymerizations were initiated using of PVC-Alk2 (synthesized from a $PVC-N_3$ containing 1.4% of azide units). a) determined by $^1$H NMR.

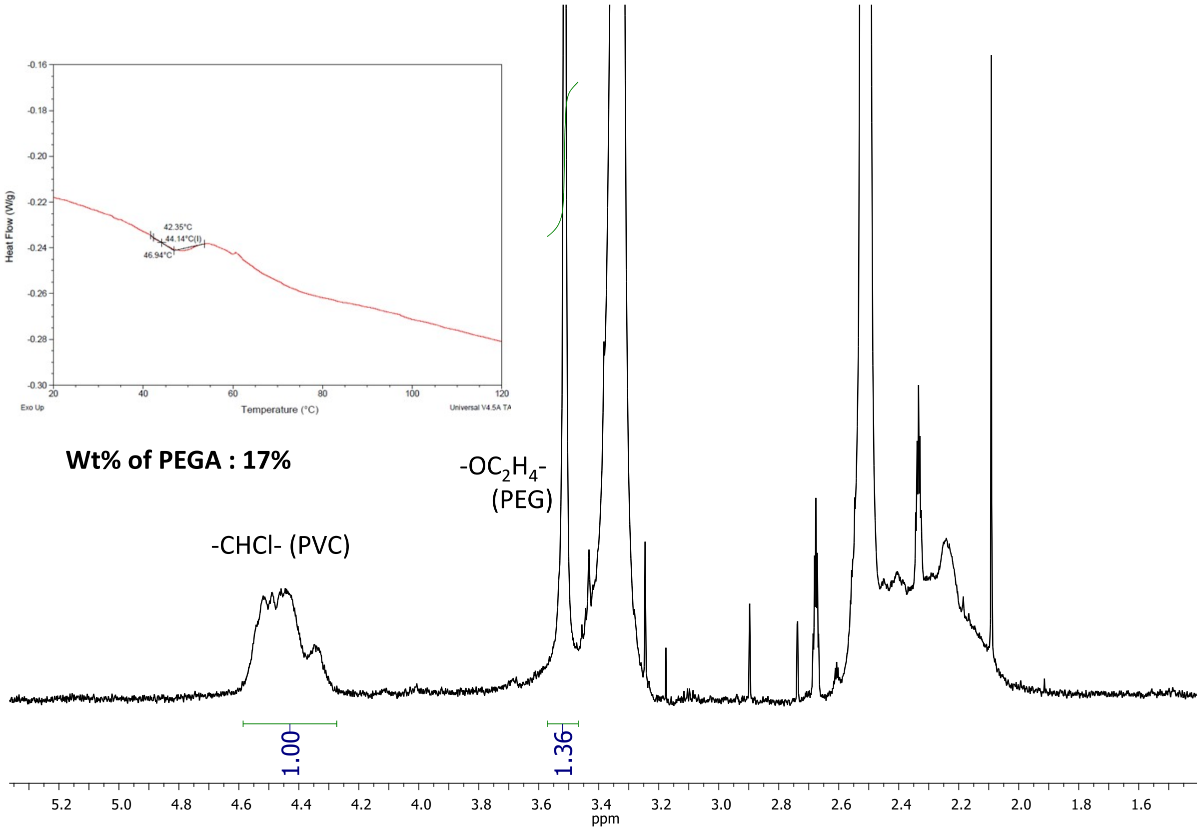


**Figure S15a.** $^1$**H NMR spectrum and DSC thermogram of PVC-*g*-PEGA containing 17 wt% of PEGA.**

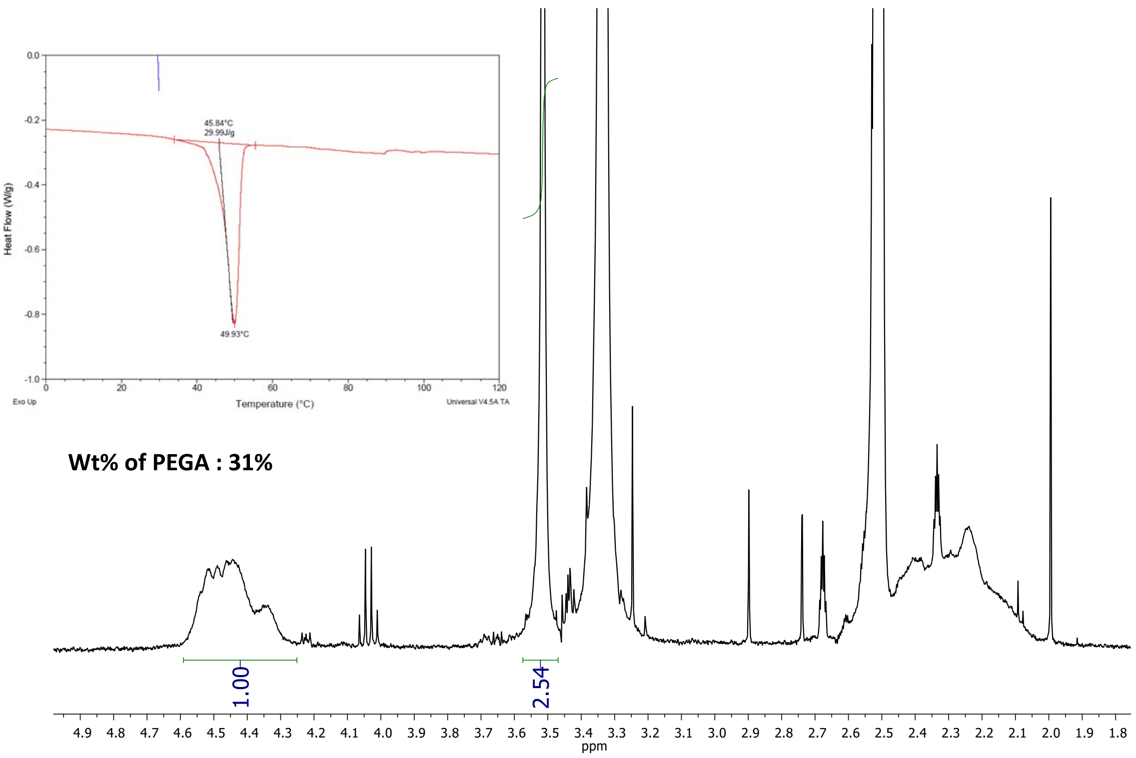


**Figure S15b.** $^1$H NMR spectrum and DSC thermogram of PVC-*g*-PEGA containing 31 wt% of PEGA.

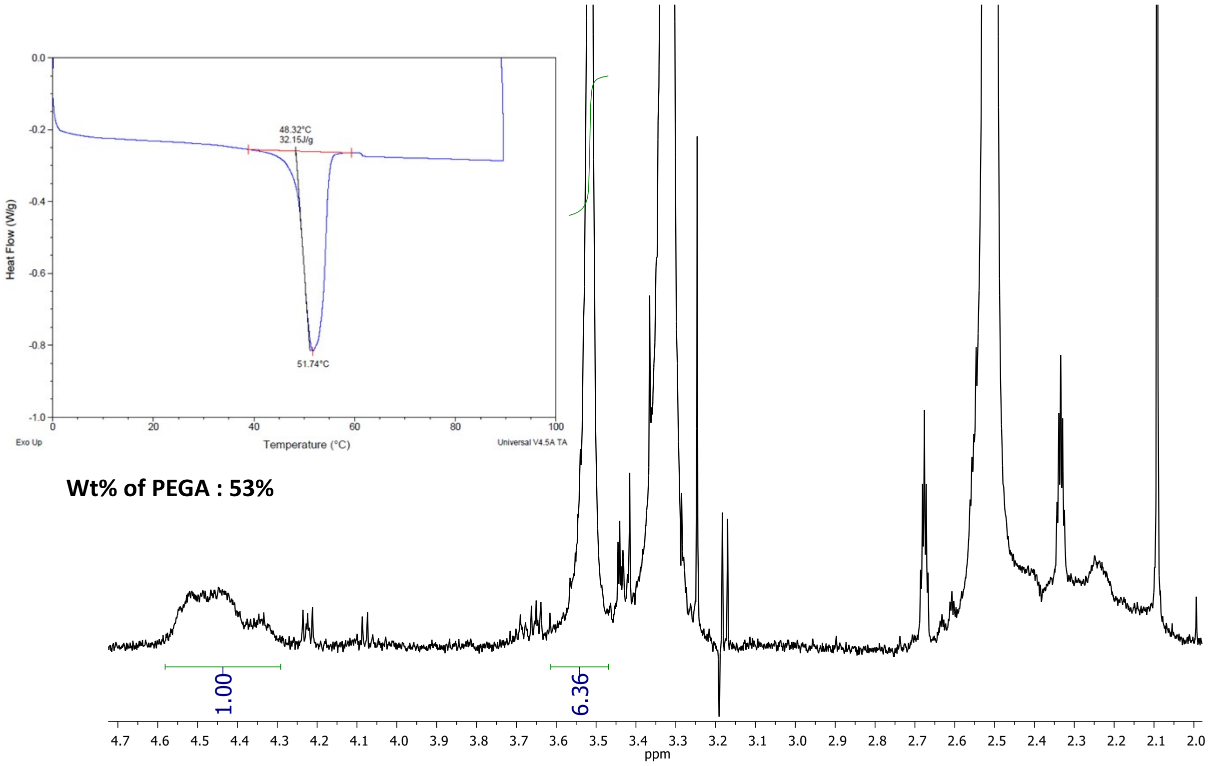


**Figure S15c.** $^1$H NMR spectrum and DSC thermogram of PVC-*g*-PEGA containing 53 wt% of PEGA.

**Table S6.** analysis of PVC-*g*-PEGA

| Integral ratio CHCl/$OC_2H_4$ $^{a)}$ | CHCl/PEGA unit ratio | DPn | wt% | $M_n$ $^{b)}$ (g/mol) | Đ $^{b)}$ | DSC $^{c)}$ | Onset E’$^{d)}$ | Onset E’’$^{d)}$ | tan δ$^{d)}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1/1.37 | 131/1 | 0.008 | 17% | 42800 | 1.51 | $T_g$ = 44°C | 42°C | 54°C | 67°C |
| 1/2.54 | 71/1 | 0.014 | 31% | 45500 | 1.57 | $T_m$ = 46°C | -11°C | -2°C | 24°C |
| 1/6.36 | 28/1 | 0.034 | 53% | 42800 | 1.51 | $T_m$ = 50°C | - | - | - |

[a] Determined by $^1$H NMR (see Figures in SI); [b] determined by SEC in THF using PS calibration; [c] determined by DSC (see Figures in SI); [d] determined by DMA

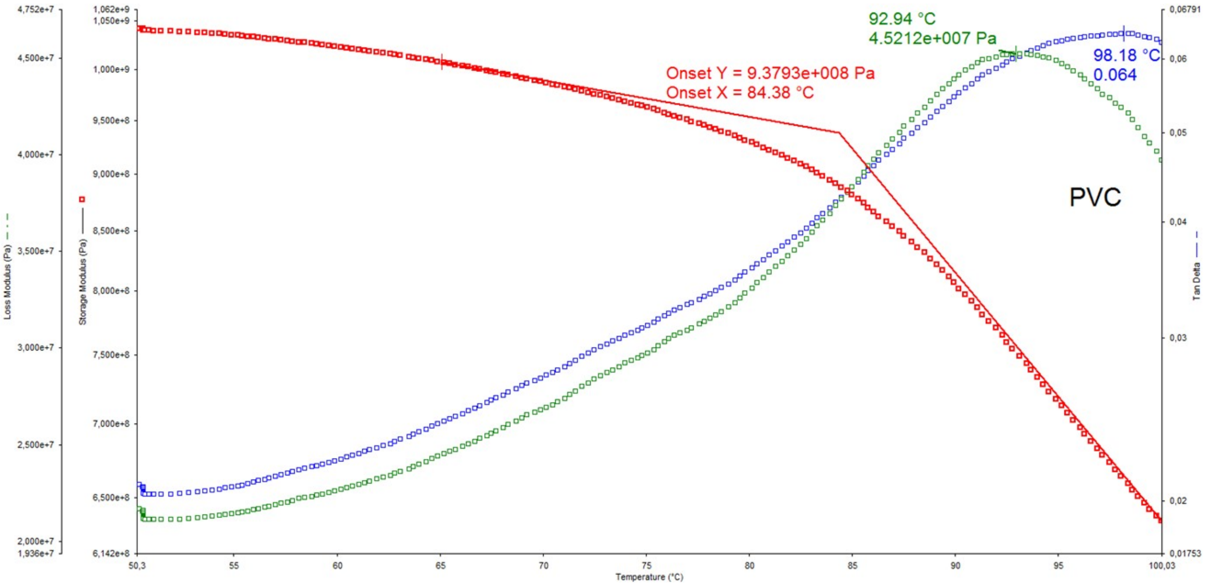


**Figure S16a DMA of PVC: evolution of the storage modulus (E'), the loss modulus (E") and the Tangent δ in function of the temperature**

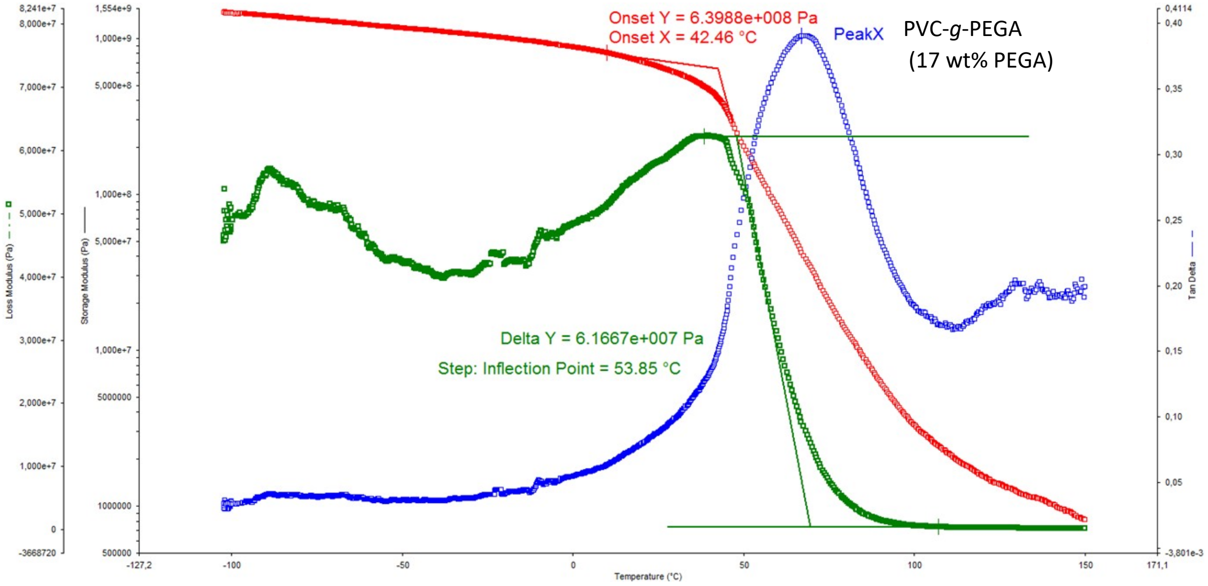


**Figure S16b DMA of PVC-*g*-PEG (17 wt% of PEGA): evolution of the storage modulus (E'), the loss modulus (E") and the Tangent δ in function of the temperature**

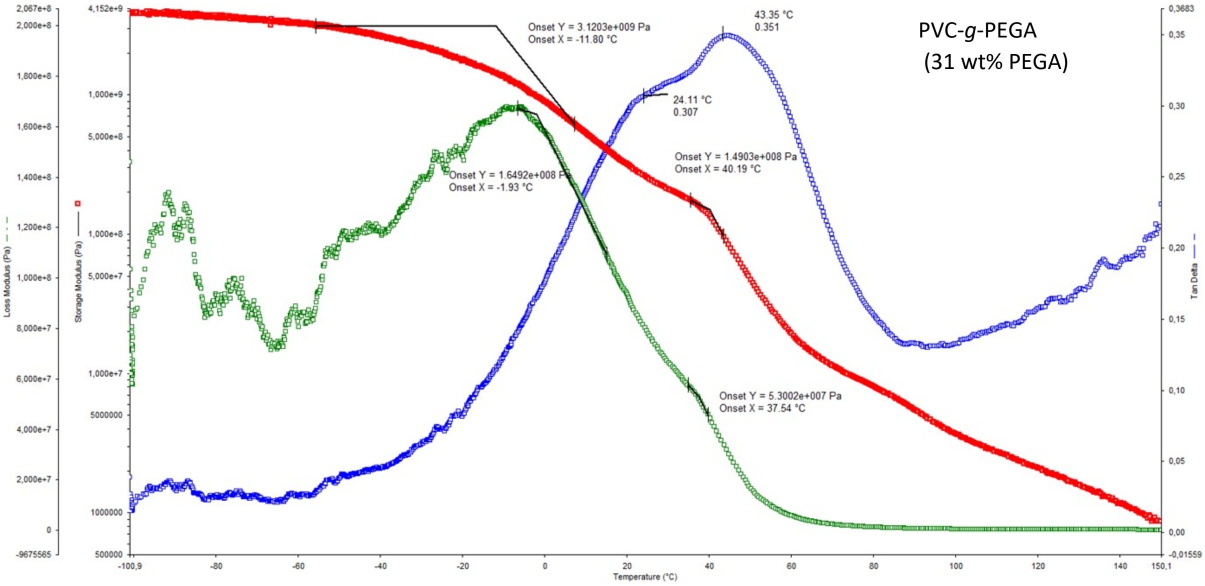


**Figure S16c DMA of PVC-*g*-PEG (31 wt% of PEGA): evolution of the storage modulus (E'), the loss modulus (E") and the Tangent δ in function of the temperature (the analysis was repeated).**

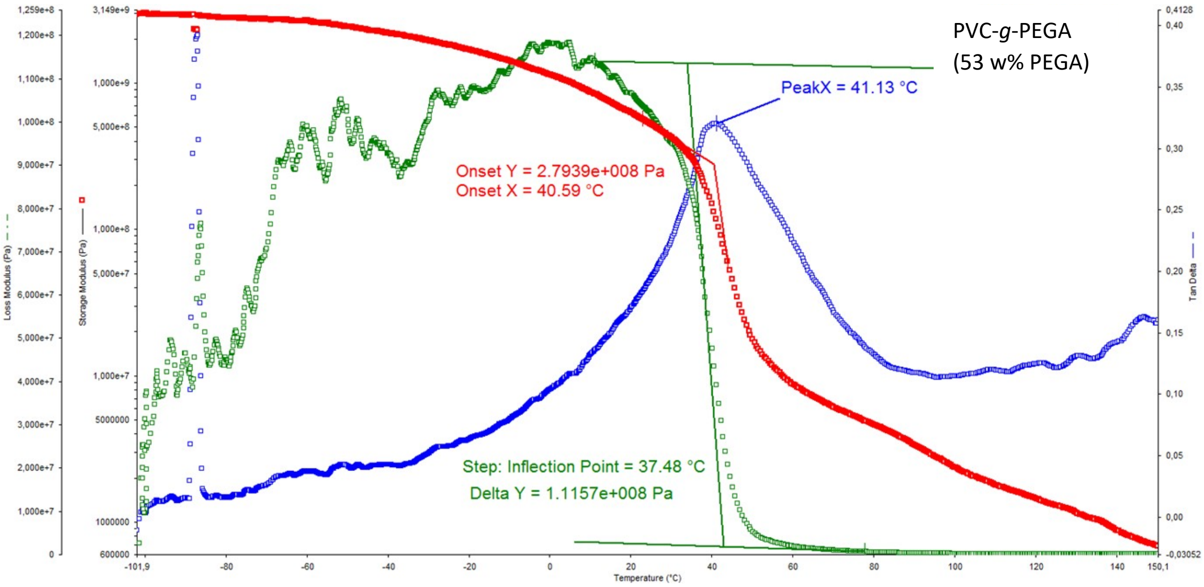


**Figure S16d DMA of PVC-*g*-PEG (53 wt% of PEGA): evolution of the storage modulus (E'), the loss modulus (E") and the Tangent δ in function of the temperature**

## References

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