

Electronic Supplementary Information

Ethylene/Vinyl Acetate-based Macrocycles via Organometallic-Mediated Radical Polymerization and CuAAC ‘Click’ Reaction.

Jérémy Demarteau,^a Julien De Winter,^b Christophe Detrembleur,^a and Antoine Debuigne*^a

^a Centre for Education and Research on Macromolecules (CERM), CESAM Research Unit, Department of Chemistry, University of Liege, Allée de la Chimie B6A, 4000 Liège, Belgium.

^b Organic Synthesis and Mass Spectrometry Laboratory, University of Mons (UMons)7000 Mons, Belgium

EXPERIMENTAL PART

Materials. All manipulations were performed by classical Schlenk techniques under argon. Vinyl acetate (VAc, >99%, Aldrich), toluene (>99%, VWR) and isoprene (>99%, Aldrich) were dried over calcium hydride, degassed by several freeze–thawing cycles before distillation under reduced pressure, and stored at -20 °C under argon. Ethylene (N35, 99.95%) was purchased from Air Liquide and used as received. The organocobalt(III) adduct initiator [BrCH₂-Co(acac)₂] was prepared as described previously¹ and stored as a ethyl acetate solution at -20 °C under argon. Sodium azide (NaN₃, Aldrich), dimethylformamide (DMF, >99%, Across), 1,6-heptadiyne (97%, Aldrich), N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), tin(II) 2-ethylhexanoate (SnOct₂, Aldrich, 95%), aluminium oxide 504C (Al₂O₃, Aldrich), potassium hydroxide (KOH, Acros), methanol (MeOH, >99%, VWR) and tetrahydrofuran (THF, >99%, VWR) were used as received. Copper bromide (CuBr, Aldrich, 98%) was purified by glacial acetic acid for 1 day, then filtered and washed 5 times with acetic acid and 5 times with ethanol before drying under vacuum and stored in a dessicator.

Characterizations. The number-average molar masses (M_n) and dispersity (\mathcal{D}) of copolymers were determined by size exclusion chromatography (SEC) in tetrahydrofuran (THF) at 45 °C at a flow rate of 1 mL/min. The apparatus is a Viscotek 305 TDA liquid chromatograph equipped with two PSS SDV analytical linear M 8 mm columns protected by a PL gel 5 μ m guard column and calibrated with polystyrene standards.

All NMR experiments were carried out at 298 K. ¹H NMR spectra of reaction mixtures for the determination of the conversions were recorded in CDCl₃ with a 400 MHz Bruker spectrometer.

Fourier transform infrared (FT-IR) spectra were measured by using a Nicolet IS5 spectrometer (Thermo Fisher Scientific) equipped with a transmission or with a diamond attenuated transmission reflectance (ATR) device. Spectra were obtained in transmission or ATR mode as a result of 32 spectra in the range of 4000–500 cm⁻¹ with a nominal resolution of 4 cm⁻¹. Spectra were analyzed with an ONIUMTM (Thermo Fisher Scientific) software.

The Matrix-Assisted Laser Desorption/Ionization Time-of-Flight (MALDI-ToF) mass spectrum was recorded using a Waters QToF Premier mass spectrometer equipped with a Nd:YAG laser using the 3rd harmonic with a wave length of 355 nm. In the context of this study, a maximum output of ~65 J is delivered to the sample in 2.2 ns pulses at 50 Hz repeating rate. Time-of-flight mass analyses were performed in the reflection mode at a resolution of about 10 000. The matrix, α -cyano-4-hydroxycinnamic acid (α -cyano), was prepared as a saturated solution in acetone. The matrix solution (1 μ L) was applied to a stainless steel target and air-dried. Polymer samples were dissolved in Methanol:Acetonitrile (1:9) to obtain 1 mg/mL solutions and 20 μ L of NaI solution (2 mg/mL in acetonitrile) are added as source of cationization agent. Then, 1 μ L aliquots of these solutions were applied onto the target area (already bearing the matrix crystals) and then air-dried.

Typical procedure for the Controlled Synthesis of α,ω -dibrominated Linear Polyvinylacetate Precursors by CMRP (Br-PVAc-Br). A solution of BrCH₂-Co(acac)₂ adduct initiator (14.5 ml in EtOAc of a 0.062 M stock solution, 0.9 mmol) was transferred into a 50 ml round-bottom flask under argon and dried under vacuum at room temperature. Dried and degassed VAc (10.0 ml, 108 mmol) were added under argon and the mixture is heated at 40 °C under 500 rpm stirring. Samples were withdrawn to determine the monomer conversion by ¹H NMR in CDCl₃ and for SEC analysis in THF (samples for SEC are deactivated by the addition of an excess of propanethiol²). Once the targeted molar mass was reached, CMRC was applied with the addition of an excess of degassed and dried isoprene (2.0 ml, 20 mmol). The reaction was stirred at room temperature for 1 day. The excess of VAc and isoprene were evaporated under reduced pressure and the dried polymer was solubilized in a 5 ml of MeOH for dialysis (cut-off = 3500 Da) in MeOH. The resulting polymer was dried and characterized by SEC in THF and by NMR (yield = 1120 mg, M_p SEC = 7770 g/mol, M_n SEC = 6440 g/mol, D = 1.14, M_n NMR = 6817 g/mol).

Typical procedure for the Controlled Synthesis of α,ω -dibrominated Linear Ethylene/Vinyl Acetate Copolymer Precursors by CMRP (Br-EVA-Br). The same procedure than for PVAc was applied for EVA copolymers (18 ml of R-Co^{III} solution in EtOAc of a 0.062 M stock solution, 1.1 mmol and V_{VAc} = 10 ml), except that the R-Co^{III}/VAc solution was transferred in a 30 ml stainless steel reactor and filled of 50 bar of ethylene followed by heating at 40 °C. After 24 h, the reactor was depressurized and filled with Ar in order to withdraw a sample under protective atmosphere for determining the VAc conversion (14 %). Then, an excess of degassed and dried isoprene (2.0 ml, 20 mmol) was added on the mixture. After purification procedure, the resulting polymer was dried and characterized by SEC in THF and by NMR (yield = 716 mg, M_p SEC = 8060 g/mol, M_n SEC = 6600 g/mol, D = 1.17, M_n NMR = 5260 g/mol).

Typical procedure for the Controlled Synthesis of α,ω -dibrominated Linear PVAc-*b*-EVA-*b*-PVAc Copolymer Precursors by CMRP (Br-PVAc-*b*-EVA-*b*-PVAc-Br). The same procedure than for PVAc was applied for EVA copolymers (13.5 ml of R-Co^{III} solution in EtOAc

of a 0.046 M stock solution, 0.6 mmol and $V_{\text{VAc}} = 10$ ml), except that the R-Co^{III}/VAc solution was transferred in a 30 ml stainless steel reactor before pressurization with 50 bar of ethylene at 40 °C. The first block of PVAc was synthesized after 4 h (12 % conversion). Then, the chain-extension by the second EVA-based block was formed until 22 % conversion in VAc by applying a pressure of 50 bar of ethylene. After 24 h, the reactor was depressurized, filled with Ar and an excess of degassed and dried isoprene (2.0 ml, 20 mmol) was added on the mixture. After purification procedure, the resulting polymer was dried and characterized by SEC in THF and by NMR (yield = 380 mg, $M_{\text{p SEC}} = 5040$ g/mol, $M_{\text{n SEC}} = 3470$ g/mol, $D = 1.28$, $M_{\text{n NMR}} = 4560$ g/mol).

Typical procedure for the Functionalization of the Linear Polymer Precursors by NaN₃ (N₃-PVAc-N₃). 850 mg of dried linear Br-PVAc-Br precursor ($M_{\text{n NMR}} = 6817$ g/mol, 0.125 mmol) was placed into a conditioned 50 ml round-bottom flask and solubilized in 10 ml of degassed DMF. A solution of 5 ml of degassed DMF and sodium azide (65 mg, 1.0 mmol) was degassed under argon for 30 min and transferred into the 50 ml round-bottom flask. The mixture turned from clear yellow to clear blue and was then stirred at 40°C overnight. The solvent was removed under vacuum at 80 °C and the polymer was solubilized in THF, which induced the precipitation of the NaBr salts. After centrifugation, the clear yellow solution was dried under vacuum at 60 °C overnight and the functionalized polymer was analyzed by SEC and NMR (yield = 815 mg, $M_{\text{p SEC}} = 7900$ g/mol, $M_{\text{n SEC}} = 6660$ g/mol, $D = 1.13$, $M_{\text{n NMR}} = 6740$ g/mol).

Typical procedure for the Formation of Cyclic Polymers by Copper(I)-catalyzed Alkyne-Azide Cycloaddition (CuAAC) click chemistry. A solution of N,N,N',N''-pentamethyldiethylenetriamine (PMDETA) (206 mg, 1.2 mmol) in dried toluene (500 ml) was bubbled with Ar for 30 min in a 1 L round-bottom flask. Cu(I)Br (170 mg, 1.2 mmol) was solubilized in a 25 ml round bottom flask, the solution was bubbled under argon for 30 min and added in the 1 L round-bottom flask. In a separate Schlenck a solution of telechelic azide-terminated PVAc (80 mg, 0.012 mmol) (N₃-PVAc-N₃) and 1,6-heptadiyne (0.014 mmol, 1.15 eq as compared to N₃-PVAc-N₃) in 10 ml of toluene was cooled in an ice cool bath at 0°C and degassed by bubbling Ar for 10 min. The degassed solution of the polymer and 1,6-heptadiyne was transferred into a gas-tight syringe and added at a rate of 0.3 mL/h to the solution of PMDETA and Cu(I)I whilst stirred. After complete addition, the solution was stirred over 24 h. The copper salts were quenched in solution by Sn(Oct)₂ in order to keep the copper in its primary oxidation state. The product was purified on alumina column first in toluene and then eluted in THF in order to remove copper residues. The solvent was evaporated by rotavap. After removing the solvent, the cyclic polymer was analyzed by FT-IR, SEC and MALDI-ToF ($M_{\text{p SEC}} = 5640$ g/mol).

Determination of the percent cyclic product formed by CuAAC cyclisation. According to the literature,³ the yield of cyclisation was determined by Equation (1):

$$\% \text{Cyclic}_{exp} = \left(\frac{\text{Cyclic peak area}}{\text{Total peak area}} \right) \times 100 \quad (1)$$

Typical procedure for the Hydrolysis of Cyclic Polymers by methanolysis. In a round-bottom flask, the cyclic PVAc (40 mg, 0.006 mmol) was solubilized in a KOH (14 mg, 0.250 mmol) solution in MeOH (5 ml). The mixture was stirred overnight at 40 °C. A green precipitate appeared in MeOH. The solution was poured in 20 ml of deionized water and centrifuged during 10 min at 1094 rpm (10 °C). The solution was removed from the vial and the polymer was analyzed by FT-IR.

Similarly, cyclic EVA copolymers (50 mg, 0.008 mmol) were solubilized in a KOH (15 mg, 0.285 mmol) solution in toluene (5 ml). The mixture was stirred overnight at 40 °C. The solution was poured in 20 ml of MeOH and centrifuged during 10 min at 1094 rpm (10 °C). The solution was removed from the vial and the polymer was analyzed by FT-IR.

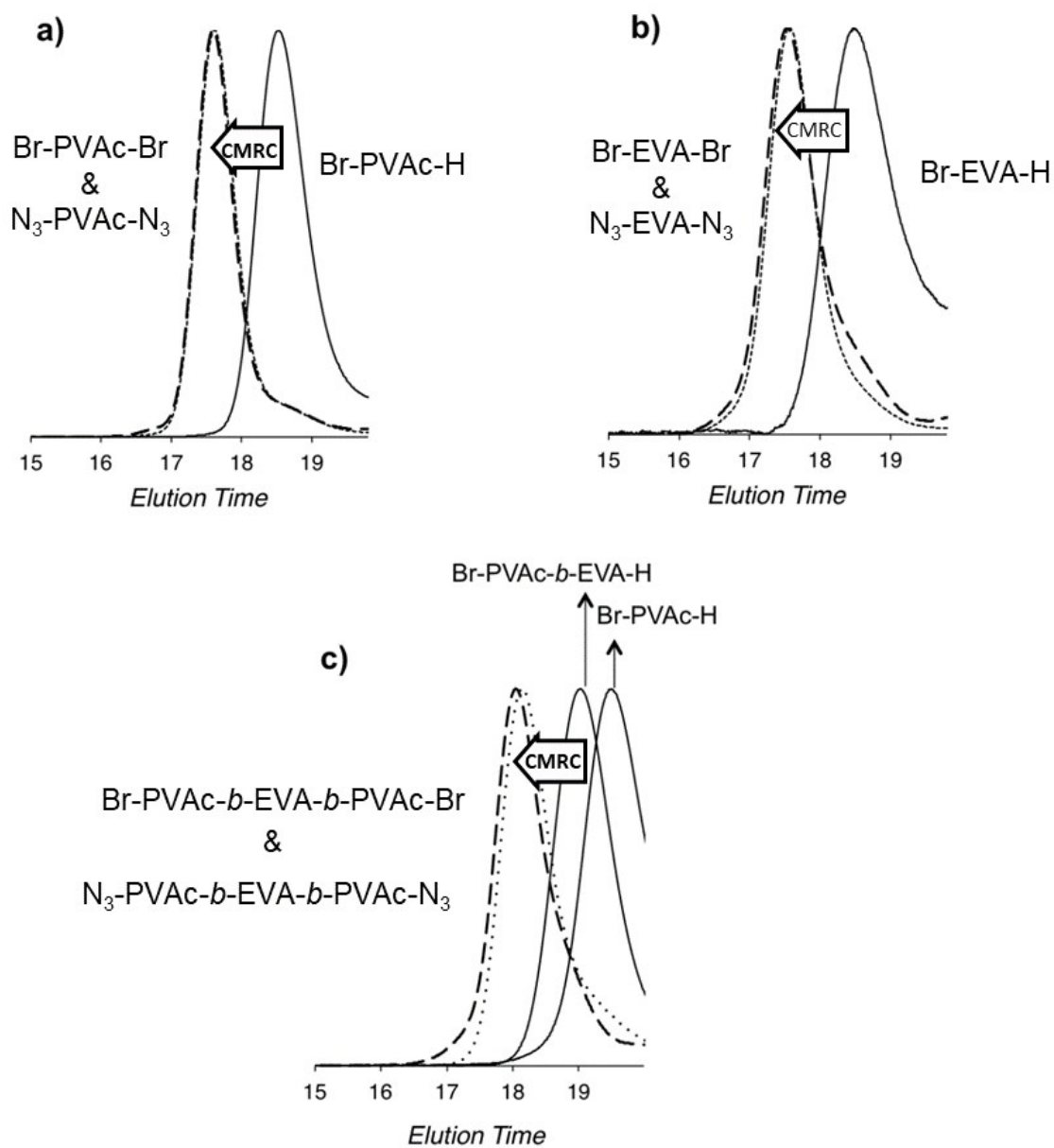


Figure S1. SEC traces of linear α -bromo (—), α,ω -dibromo (- - -) and α,ω -diazide (. . . .) (co)polymers based on PVAc (a), EVA (b) and PVAc-*b*-EVA (c). (Table 1)

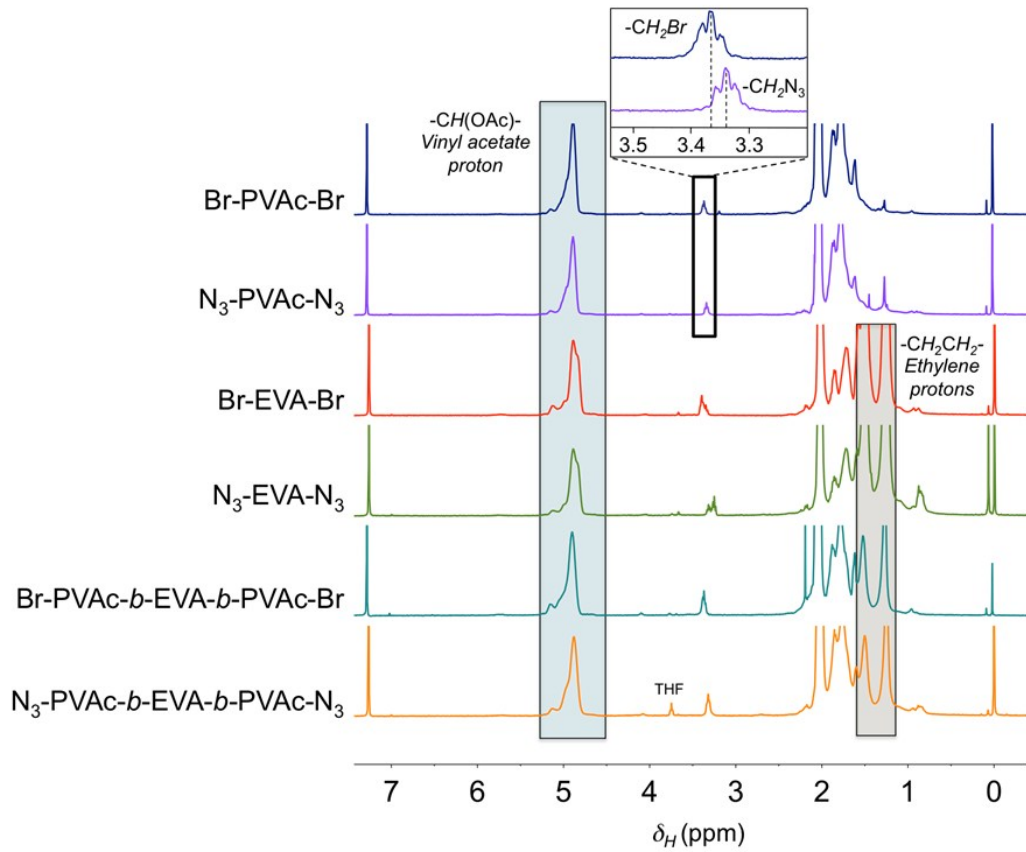


Figure S2. ^1H NMR of of the α,ω -dibromo and α,ω -diazide (co)polymers in CDCl_3 .

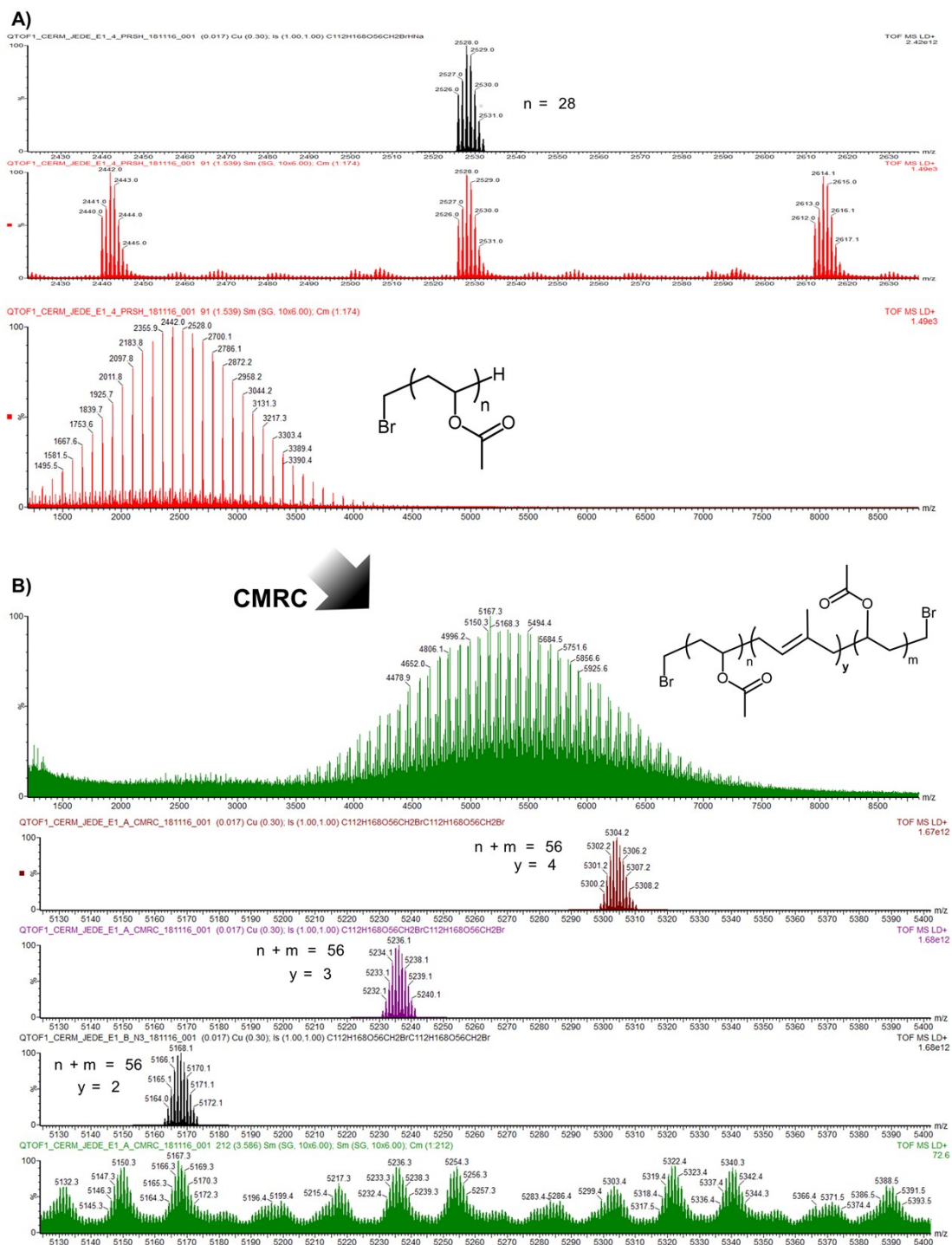


Figure S3. MALDI-ToF spectra of Br-PVAc-H (**A**) and Br-PVAc-Br (**B**) and the corresponding magnifications. The inset corresponds to the comparison between the theoretical and experimental isotopic distribution for sodiated polymers.

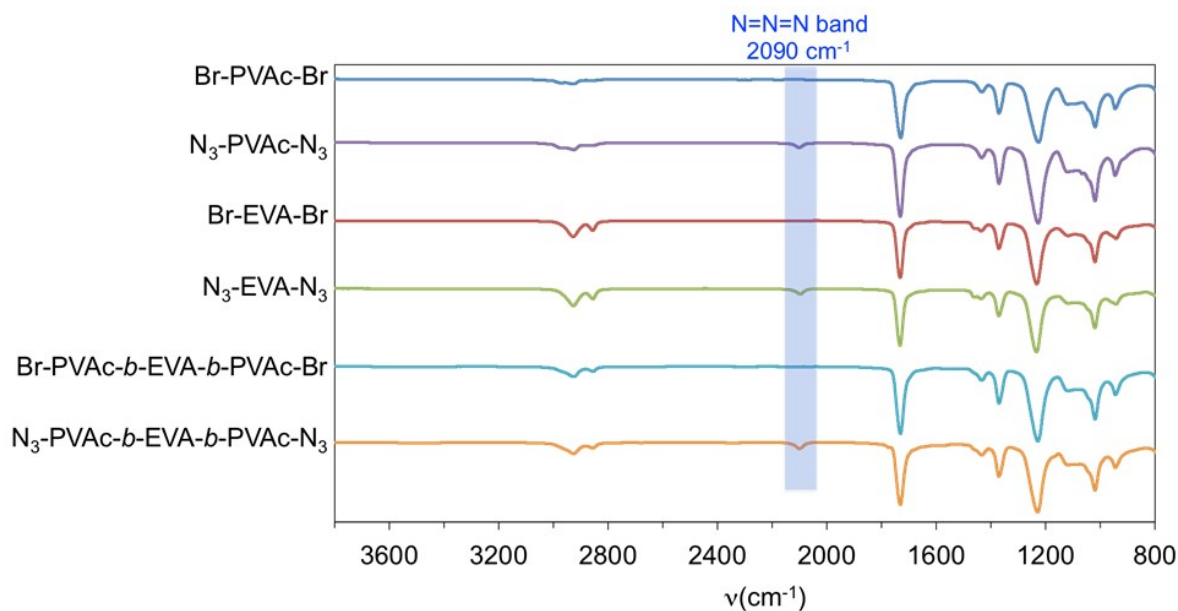


Figure S4. FT-IR of the α,ω -dibromo and α,ω -diazide (co)polymers.

References

- 1 J. Demarteau, A. Kermagoret, I. German, D. Cordella, K. Robeyns, J. De Winter, P. Gerbaux, C. Jerome, A. Debuigne and C. Detrembleur, *Chem. Commun.*, 2015, **51**, 14334–14337.
- 2 A. Debuigne, J.-R. Caille and R. Jérôme, *Macromolecules*, 2005, **38**, 5452–5458.
- 3 A. F. Voter, E. S. Tillman, P. M. Findeis and S. C. Radzinski, *ACS Macro Lett.*, 2012, **1**, 1066–1070.