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Zhuoqun Wang, Rinaldo Poli, Christophe Detrembleur, Antoine Debuigne. Organometallic-Mediated Radical (Co)polymerization of γ -Methylene- γ -Butyrolactone: Access to pH-Responsive Poly(vinyl alcohol) Derivatives. *Macromolecules*, 2019, 52 (22), pp.8976-8988. 10.1021/acs.macromol.9b01838 . hal-02565062

HAL Id: hal-02565062

<https://hal.science/hal-02565062>

Submitted on 1 Mar 2021

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Organometallic-Mediated Radical (Co)Polymerization of γ -Methylene- γ -Butyrolactone: Access to pH-Responsive Poly(vinyl alcohol) Derivatives.

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KEYWORDS. Vinyl lactone, reversible deactivation radical polymerization, organometallic-mediated radical polymerization, poly(vinyl alcohol), pH-responsive.

ABSTRACT. Conjugated vinyl lactones commonly serve as precursors of polymers with pendant cyclic esters, which can undergo several chemical modifications. They have notably been copolymerized with “more activated monomers” (MAMs) like (meth)acrylates. By contrast, the radical polymerization of the non-conjugated methylene lactone analogs has been disregarded as well as their copolymerization with “less activated monomers” (LAMs) such as acyclic vinyl esters. The present work explores the conventional radical polymerization and the reversible deactivation radical polymerization of γ -methylene- γ -butyrolactone (γ M γ BL) and its copolymerization with vinyl acetate (VAc). Statistical P(γ M γ BL-*co*-VAc) copolymers with predictable molar mass, low dispersity and precise compositions were notably achieved by organometallic-mediated radical polymerization based on cobalt complexes via both reversible termination (RT), also referred to as

reversible chain deactivation, and degenerative chain transfer (DT) pathways. Upon hydrolysis, these γ M γ BL-containing (co)polymers release one alcohol moiety and one carboxylic group per repeating unit leading to unprecedented carboxylic acid-functionalized poly(vinyl alcohol) derivatives. A preliminary study emphasizes the pH-responsiveness of the latter in water.

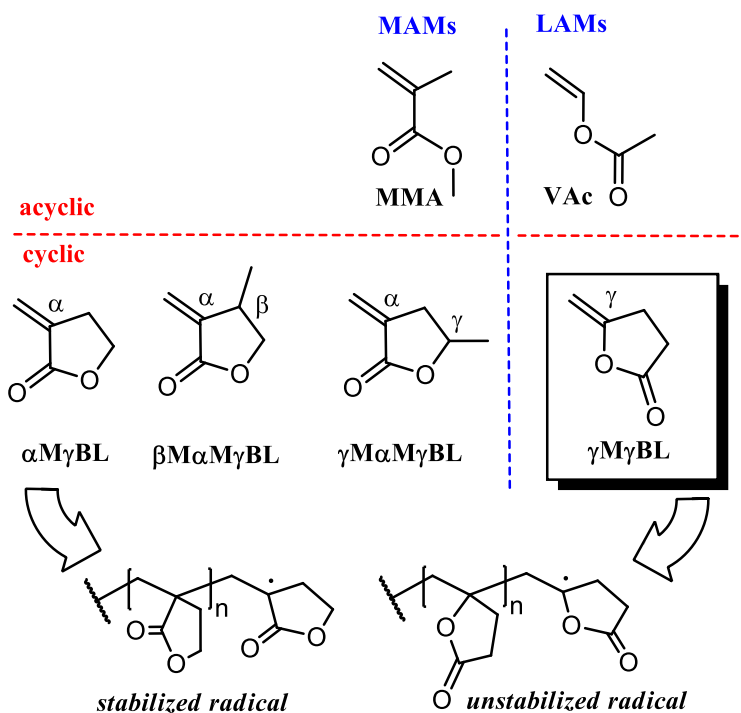
INTRODUCTION

Vinylidene lactones have received great interest in the last decade as building blocks for the production of bio-based specialty polymers.¹ Among them, α -methylene- γ -butyrolactone (α M γ BL),¹ or tulipalin A, can be isolated from tulips whereas β -methyl- α -methylene- γ -butyrolactone (β M α M γ BL)² and γ -methyl- α -methylene- γ -butyrolactone (γ M α M γ BL)³ are prepared from biomass-derived itaconic acid and levulinic acid, respectively (Scheme 1). Several approaches have been considered for the conversion of these methylene lactones into (co)polymers including ring opening polymerization⁴⁻⁶ leading to polyesters but also group transfer,^{7,8} anionic,⁹ zwitterionic,¹⁰⁻¹⁴ coordination¹⁵⁻¹⁸ and radical¹⁹⁻²⁵ polymerizations providing polymers with pendant five-membered ring.

The radical polymerization of the methylene lactones has been largely investigated and occurs via repeated radical addition onto their exo-cyclic double bond (Scheme 1). In this respect, α M γ BL derivatives can be considered as cyclic analogs of the petroleum-based methyl methacrylate (MMA). As a matter of fact, it belongs to the class of more activated monomers (MAMs), which consist in conjugated monomers bearing a radical stabilizing group onto the double bond. Homopolymers with pendant butyrolactone moieties were notably prepared via conventional radical polymerization of α M γ BL^{19,20} and β M α M γ BL²¹. Compared to PMMA, these

poly(α M γ BL)s exhibit higher T_g as well as increased optical properties.^{19,26} The conventional radical copolymerization of α M γ BL^{22,23,27–29} or γ M α M γ BL^{24,25} with various conjugated vinyl monomers like MMA,^{22–24} styrene,^{22,24,28} acrylamide,²⁷ butyl acrylate,²⁴ exomethylene lactide²⁵ and methacrylated oleic acid,²⁹ is also reported. Interestingly, these α -methylene lactones exhibit greater reactivity compared to their acyclic MMA counterpart due to the higher degree of delocalization of their radical species onto the carbonyl group of the rigid lactone.²¹

The synthesis of well-defined α -methylene lactone-based (co)polymers was also achieved via reversible deactivation radical polymerization (RDRP). For example, α M γ BL-containing homopolymers³⁰ and block copolymers^{30–33} with predictable molar masses and low dispersities were prepared via copper catalyzed atom transfer radical polymerization (ATRP). High-density poly(α M γ BL) brushes were also produced by surface-initiated ATRP of α M γ BL.³⁴ On the other hand, α M γ BL as well as its γ -substituted derivatives were polymerized in a controlled manner via reversible addition fragmentation chain transfer (RAFT).³⁵ The RAFT polymerization of γ M α M γ BL and copolymerization with styrene was also performed under miniemulsion³⁶ and from ab initio emulsion³⁷ conditions.



Scheme 1. Radical polymerization of conjugated and non-conjugated methylene- γ -butyrolactones.

Considering the higher reactivity of α M γ BL-based monomers compared to MMA,²¹ their copolymerization with unconjugated Less Activated Monomers (LAMs) including vinyl acetate (VAc) or α -olefins is clearly jeopardized. However, γ -methylene- γ -butyrolactone (γ M γ BL), a cyclic structural analog of VAc, appears as an ideal candidate for incorporating pendant lactones within LAMs-based copolymers (Scheme 1). Surprisingly, γ M γ BL has almost been completely disregarded in the polymerization field. To our knowledge, only one example relative to the tentative conventional radical copolymerization of γ M γ BL and MMA is succinctly mentioned in the literature²³ and the reversible deactivation radical (co)polymerization of γ M γ BL has never been reported. In the present work, we explored for the first time the conventional radical homopolymerization of γ M γ BL as well as its copolymerization with VAc. Reactivity ratios were

determined to gain insight into the distribution of the cyclic and acyclic ester moieties along the backbone. The reversible deactivation radical copolymerization of γ M γ BL with VAc was also investigated through organometallic-mediated radical polymerization (OMRP),^{38–41} an efficient RDRP technique for controlling the polymerization of several LAMs including vinyl esters,^{42–44} vinyl amides,^{45–48} vinyl carbonates,^{49,50} vinyl chloride,⁵¹ vinylidene fluoride⁵² or ethylene^{53–55}. Copolymerization conditions were optimized to produce poly(γ M γ BL-*co*-VAc) with predictable molar mass, low dispersity and precise composition. Finally, some post-polymerization modifications of these poly(γ M γ BL-*co*-VAc) were carried out in order to produce unprecedented carboxylic acid-functionalized poly(vinyl alcohol)s (PVA) via hydrolysis of the pendant acyclic and cyclic esters. A preliminary study of the solution properties of these potentially pH-responsive polymers was also performed.

EXPERIMENTAL SECTION

Materials.

Cobalt(II) acetylacetonate (Co(acac)₂) (97%, Acros), 4-pentynoic acid (98%, Fluorochem), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) (98%, Aldrich), 2,2'-azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70, $t_{1/2}$ = 10 h at 30 °C) (> 98 %, Wako), 2,2'-azobisisobutyronitrile (AIBN) (AIBN, $t_{1/2}$ = 10 h at 65 °C) (98 %, Aldrich) were used as received. Sodium hydroxide (NaOH, \geq 97%, Acros), silica gel for column chromatography (60 Å, ROCC S.A.), tetrahydrofuran (THF, \geq 99.9 %, VWR), chloroform (> 99%, VWR), methanol (MeOH, \geq 99.8 %, VWR), n-heptane (> 99.6 %, VWR), n-hexane (> 99%, VWR), ethyl acetate (\geq 99.9%, VWR), acetonitrile (\geq 99.99 %, Acros) were used as received. N,N-dimethylformamide (DMF, > 99%, VWR) were

dried over molecular sieves prior to use. Dichloromethane (CH_2Cl_2) was degassed and dried over 4 Å molecular sieves. Vinyl acetate (VAc) (> 99%, Aldrich) was dried under calcium hydride, purified by distillation under reduced pressure and degassed by freeze-drying cycle under vacuum. The alkyl-cobalt (III) adduct initiator ($\text{PVAc}_{<4}\text{-Co(acac)}_2$, $[\text{Co(acac)}_2\text{-(CH(OAc)-CH}_2\text{)}_{<4}\text{R}_0]$; R_0 being the primary radical generated by 2,2'-azo-bis(4-methoxy-2,4-dimethyl valeronitrile) (V-70, Wako) was prepared as described previously⁴³ and stored as a CH_2Cl_2 solution at $-20\text{ }^\circ\text{C}$ under argon. Dialyses were carried out with Spectra/Por Dialysis Membrane (Pre-treated RC Tubing 1 kDa).

Characterization. Size exclusion chromatography (SEC) of $\text{P}\gamma\text{M}\gamma\text{BL}$ and of $\text{P}(\gamma\text{M}\gamma\text{BL-co-VAc})$ with $F_{\gamma\text{M}\gamma\text{BL}} > 0.5$ were carried out in DMF containing 0.025 M of LiBr at $55\text{ }^\circ\text{C}$ with a Waters chromatograph equipped with three columns (Waters Styragel PSS GRAM 1000Å ($\times 2$), 30Å), a dual λ absorbance detector (Waters 2487) and a refractive index detector (Waters 2414). The system was operated at a flow rate of 1 mL/min. A polystyrene calibration was used. SEC analyses of $\text{P}(\gamma\text{M}\gamma\text{BL-co-VAc})$ with $F_{\gamma\text{M}\gamma\text{BL}} < 0.5$ were carried out in THF at $45\text{ }^\circ\text{C}$ at a flow rate of 1 mL/min with a Viscotek 305 TDA liquid chromatograph equipped with 2 PSS SDV linear M columns calibrated with PS. ^1H NMR, HSQC and COSY spectra were recorded at 298 K with a Bruker Avance III HD spectrometer ($B_0 = 9.04\text{ T}$) (400 MHz) and treated with MestreNova software. IR spectra were recorded on ThermoFischer Scientific Nicolet IS5 equipped with an ATR ID5 module using a diamond crystal ($650\text{ cm}^{-1}\text{-}4000\text{ cm}^{-1}$). Differential scanning calorimetry (DSC) was performed on a TA Instruments Q1000 DSC, using hermetic aluminium pans, indium standard for calibration, nitrogen as the purge gas, a sample weight of about 5 mg. The sample was cooled down to $-40\text{ }^\circ\text{C}$ at $40\text{ }^\circ\text{C}/\text{min}$ cooling rate, followed by an isotherm at $-40\text{ }^\circ\text{C}$ for 2 min and heating up to $120\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C}/\text{min}$ heating rate. This cycle was repeated twice. TGA analyses were

carried out with a Hi-Res TGA Q500 from TA Instruments under nitrogen at a heating rate of 20 °C/min from ambient temperature to 600 °C at a heating rate of 20 °C/min.

Computational details.

The computational work was carried out using the Gaussian09 suite of programs.⁵⁶ Gas-phase geometry optimizations were performed without any symmetry constraint using the BPW91* functional, which is a reparametrized version of B3PW91 with the same parameters previously optimized for B3LYP,⁵⁷ and the 6-311G(d,p) basis functions for all light atoms (H, C, O, Si), whereas the Co atom was treated with the SDD basis set augmented by an f polarization function ($\alpha = 2.780$)⁵⁸ A correction for dispersion was also included during the geometry optimizations using Grimme's D3 empirical method (BPW91*-D3), using SR6 and S8 parameters identical to those optimized for B3PW91.⁵⁹ The unrestricted formulation was used for open-shell molecules, yielding only minor spin contamination ($\langle S^2 \rangle$ at convergence was very close to the expected values (0.75 for doublet states and 3.75 for the quartet state). All final geometries were characterized as local minima by verifying that all second derivatives of the energy were positive. Thermochemical corrections were obtained at 298.15 K on the basis of frequency calculations, using the standard approximations (ideal gas, rigid rotor and harmonic oscillator). A further correction of 1.95 Kcal/mol was applied to bring the G values from the gas phase (1 atm) to the solution (1 mol/L) standard state.⁶⁰ The Cartesian coordinates and energies of all optimized structures are available in the Supporting Information (Table S5).

Synthesis of γ -methylene- γ -butyrolactone (γ M γ BL). 4-Pentynoic acid (2.00 g, 20.4 mmol) and Pd(OAc)₂ (0.023 g, 0.10 mmol) were placed under argon in a 100 mL flask and dissolved in degassed CHCl₃ (30 mL). The reaction mixture was then heated at 50 °C under stirring for 24 h. After cooling the reaction mixture to room temperature, CHCl₃ was evaporated under reduced

pressure. The reaction mixture was purified by column chromatography (hexane/ethyl acetate: 7/3 (v/v), R_f of $\gamma\text{M}\gamma\text{BL}$ = 0.58). Accordingly, $\gamma\text{M}\gamma\text{BL}$ was collected as a colorless liquid (1.47 g) in a 73 % yield. ^1H NMR (400 MHz, CDCl_3): δ 4.74 (d, J = 2.3 Hz, 1H), 4.32 (d, J = 2.0 Hz, 1H), 2.94-2.85 (m, 2H), 2.73-2.58 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 174.92, 155.70, 88.64, 29.84, 25.06. IR (cm^{-1}) 2927, 1802, 1668, 1445, 1292, 1119, 1005, 968, 881, 838, 662.

Conventional radical polymerization of $\gamma\text{M}\gamma\text{BL}$. AIBN (0.082 g, 0.50 mmol) and $\gamma\text{M}\gamma\text{BL}$ (0.98 g, 10 mmol) were placed in a 15 mL Schlenk tube, degassed by three freeze-pump-thaw cycles and placed under argon, then heated at 70 °C. After 24 h, samples were withdrawn for determining the molecular parameters (M_n , D) by SEC in DMF using a PS calibration. The conversion was determined by gravimetry. The homopolymer was dissolved in acetonitrile and purified via repeated precipitations (three times) in methanol and dried under vacuum overnight at 80 °C before characterization by ^1H NMR, ^{13}C NMR, HSQC and COSY in CD_3CN .

Conventional radical copolymerization of $\gamma\text{M}\gamma\text{BL}$ and VAc. V-70 (0.31 g, 1.0 mmol) and $\gamma\text{M}\gamma\text{BL}$ (0.78 g, 8.0 mmol) were placed in a 15 mL Schlenk tube, degassed by three freeze-pump-thaw cycles and placed under argon. After addition of degassed VAc (1.10 mL, 1.03 g, 12.0 mmol), the polymerization medium ($f_{\gamma\text{M}\gamma\text{BL}}^0 = 0.4$) was heated at 40 °C. After 24 h, samples were withdrawn for determining the conversion by ^1H NMR in CDCl_3 and the molecular parameters (M_n , D) by SEC in THF. The final copolymer was purified via repeated precipitations (three times) in n-heptane and dried under vacuum overnight at 80 °C before characterization by ^1H NMR, ^{13}C NMR, HSQC and COSY in CDCl_3 .

A similar experiment was carried out with a different initial comonomer feed ratio, namely $f_{\gamma\text{M}\gamma\text{BL}}^0 = 0.2$, keeping constant all other parameters (40 °C, $[\text{comonomers}]_0 / [\text{V-70}]_0 = 100/5$).

Determination of reactivity ratios for radical copolymerization of γ M γ BL and VAc. A series of γ M γ BL/VAc copolymerizations were carried out in bulk at 40 °C with different comonomer ratios ($0.1 < f^{\circ}_{\gamma\text{M}\gamma\text{BL}} < 0.7$) using V-70 as initiator ($[\text{comonomers}]_0/[\text{V-70}]_0=100/3$). Copolymerizations were stopped at low conversion in order to avoid significant composition drift. Conversions were determined by ^1H NMR in CDCl_3 . The copolymers were purified by repeated precipitation in heptane (three times) and dried at 50 °C under reduced pressure. The molar fractions of the comonomers in the copolymer ($F_{\gamma\text{M}\gamma\text{BL}}$ and F_{VAc}) were determined by ^1H NMR in CDCl_3 . These data, provided in Table S1, were then used for the determination of the reactivity ratios via three methods described below.

- (i) The Fineman-Ross linearization method⁶¹ which generates a straight line whose slope and intercept with the ordinate (Y-axis r) correspond, respectively, to r_1 and r_2 (Eq. 1).

$$f(F-1)/F = r_1 (f^2/F) - r_2 \quad (\text{Eq. 1})$$

, where $f = f_1/f_2$ and $F = F_1/F_2$

- (ii) The Kelen-Tüdös method⁶² which involves parameters η and ζ , mathematical functions of the mole ratios in the monomer feed (f) and in the copolymer (F) and of a parameter α calculated on the basis of the lowest and highest values of (f^2/F) . The determination of r_1 and r_2 is made possible by the extrapolation and the interception at $\xi=1$ and $\xi=0$, giving respectively r_1 and $(-r_2/\alpha)$ (Eq. 2).

$$\eta = (r_1 + (r_2/\alpha)) \zeta - (r_2/\alpha) \quad (\text{Eq. 2})$$

,where $\eta = (f(F-1))/(F(\alpha+(f^2/F))$; $\zeta = (f^2/F)/(\alpha+(f^2/F))$; $\alpha = ((f^2/F)_{\max} \times (f^2/F)_{\min})^{0.5}$

(iii) The non-linear least squares method^{63,64} based on the Mayo-Lewis equation (Eq. 3).

$$F_1 = (r_1 f_1^2 + f_1 f_2) / (r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2) \quad (\text{Eq. 3})$$

Based on the reactivity ratio, the Skeist's model⁶⁵ (Eq. 4 and 5) was used to predict the cumulative and instantaneous copolymer composition (F_{cumul} and F_{inst}) as a function of the monomer conversion.

$$\text{Conv} = 1 - (M/M_0) = 1 - [(f_1/f_1^\circ)^\alpha (f_2/f_2^\circ)^\beta [(f_1^\circ - \delta)/(f_1 - \delta)]^\gamma] \quad (\text{Eq. 4})$$

,where M_0 and M are the initial and the instantaneous monomer concentration, f° and f correspond to the initial and the instantaneous mole fraction in the feed and α , β , δ , γ are defined as follows: $\alpha = r_2 / (1-r_2)$; $\beta = r_1 / (1-r_1)$; $\gamma = (1-r_1 r_2) / (1-r_1) (1-r_2)$; $\delta = (1-r_2)/(2-r_1-r_2)$

$$F_{1 \text{ cumul}} = [f_1^\circ - f_1(1-\text{conv})]/\text{conv} \quad (\text{Eq. 5})$$

Organometallic-mediated radical polymerization of $\gamma\text{M}\gamma\text{BL}$ via reversible termination (RT).

$\gamma\text{M}\gamma\text{BL}$ (0.98 g, 10 mmol) was placed in a 15 mL Schlenk tube, degassed by three freeze-pump-thaw cycles and placed under argon. A solution of alkyl-cobalt(III) initiator ($\text{PVAc}_{-4}\text{-Co}(\text{acac})_2$) in CH_2Cl_2 (0.18 mL of a 0.111 M stock solution, 0.020 mmol) was added to $\gamma\text{M}\gamma\text{BL}$ followed by

evaporation of CH_2Cl_2 under reduced pressure at room temperature. The reaction mixture ($[\gamma\text{M}\gamma\text{BL}]_0/[\text{PVAc}_{<4}\text{-Co(acac)}_2]_0 = 500/1$,) was heated at $40\text{ }^\circ\text{C}$ for 24 h. After 24 h, one sample was taken and added with TEMPO (1 mg/0.1 mL of sample) in order to quench the polymerization before determining the conversion by gravimetry. Another sample was taken and dissolved in DMF (containing 10 mg of TEMPO per mL of DMF) before determining the molecular parameters (M_n , D) by SEC calibrated with polystyrene in DMF. Finally, the polymerization mixture was quenched by addition of TEMPO (0.20 g) dissolved in DMF (1 mL). The final copolymer was purified by precipitation in methanol (three times) and dried overnight under vacuum at $80\text{ }^\circ\text{C}$ before characterization via ^1H NMR, ^{13}C NMR, HSQC and COSY in CD_3CN .

Organometallic-mediated radical copolymerization of $\gamma\text{M}\gamma\text{BL}$ and VAc via reversible termination (RT). $\gamma\text{M}\gamma\text{BL}$ (0.49 g, 5.0 mmol) was placed in a 15 mL Schlenk tube, degassed by three freeze-pump-thaw cycles and placed under argon. A solution of alkyl-cobalt(III) initiator ($\text{PVAc}_{<4}\text{-Co(acac)}_2$) in CH_2Cl_2 (0.78 mL of a 0.064 M stock solution, 0.05 mmol) was added to $\gamma\text{M}\gamma\text{BL}$ followed by evaporation of CH_2Cl_2 under reduced pressure at room temperature. Finally, degassed VAc (1.84 mL, 1.72 g, 20 mmol) was injected under argon. The reaction mixture ($f^\circ_{\gamma\text{M}\gamma\text{BL}} = 0.2$ and $f^\circ_{\text{VAc}} = 0.8$, $[\text{VAc}]_0/[\gamma\text{M}\gamma\text{BL}]_0/[\text{PVAc}_{<4}\text{-Co(acac)}_2] = 400/100/1$) was heated at $40\text{ }^\circ\text{C}$ for 12 h. Samples were regularly taken and added with of TEMPO in order to quench the polymerization. The monomer conversion was determined by ^1H NMR in CDCl_3 (1 mg of TEMPO was added per mL of CDCl_3). The molecular parameters (M_n , D) of the polymer were determined by SEC in THF using a polystyrene calibration (samples were dissolved in THF containing 10 mg of TEMPO/mL of THF). After 12 h, the polymerization mixture was quenched by addition of TEMPO (0.20 g) dissolved in DMF (1 mL). The final copolymer was purified by precipitation in

n-heptane (three times) and dried overnight under vacuum at 80 °C before characterization via ^1H NMR, ^{13}C NMR, HSQC and COSY in CDCl_3 .

Similar experiments were carried out with a different monomer initiator ratios keeping constant all other parameters ($f^\circ_{\gamma\text{M}\gamma\text{BL}} = 0.2$, 40 °C, bulk): $[\text{VAc}]_0/[\gamma\text{M}\gamma\text{BL}]_0/[\text{PVAc}_{<4}\text{-Co(acac)}_2]_0 = 800/200/1$ and $200/50/1$. The initial comonomer feed ratio was also varied ($f^\circ_{\gamma\text{M}\gamma\text{BL}} = 0.4$ and 0.7) keeping constant all other parameters (40 °C, bulk, $[\text{comonomers}]_0/[\text{PVAc}_{<4}\text{-Co(acac)}_2]_0 = 500$). Note that the copolymer produced from $f^\circ_{\gamma\text{M}\gamma\text{BL}} = 0.7$ was recovered by precipitation in methanol instead of heptane.

Organometallic-mediated radical polymerization of $\gamma\text{M}\gamma\text{BL}$ via degenerative chain transfer

(DT). $\gamma\text{M}\gamma\text{BL}$ (0.98 g, 10 mmol) was placed in a 15 mL Schlenk tube. After degassing by three freeze-pump-thaw cycles, the degassed $\gamma\text{M}\gamma\text{BL}$ was transferred to a 15 mL Schlenk tube with Co(acac)_2 (0.005 g, 0.02 mmol) and AIBN (0.0099 g, 0.06 mmol) under argon. The reaction mixture ($[\gamma\text{M}\gamma\text{BL}]_0/[\text{AIBN}]_0/[\text{Co(acac)}_2]_0 = 500/3/1$) was heated at 70 °C for 24 h and samples were regularly taken from the reaction mixture and added with TEMPO in order to quench the polymerization. The monomer conversion was determined by gravimetry after addition of TEMPO (1 mg/0.1 mL of sample). The molecular parameters (M_n , D) of the polymer were determined by SEC in DMF using a polystyrene calibration (samples were dissolved in DMF containing 10 mg of TEMPO/mL of DMF). After 24 h, the polymerization mixture was quenched by addition of TEMPO (0.20 g) dissolved in DMF (1 mL). The final copolymer was purified by precipitation in methanol (three times) and dried overnight under vacuum at 80 °C before characterization via ^1H NMR, ^{13}C NMR, HSQC and COSY in CD_3CN .

A similar experiment was conducted at 40 °C using V-70 instead of AIBN ($[\gamma\text{M}\gamma\text{BL}]_0/[\text{V-70}]_0/[\text{Co}(\text{acac})_2]_0 = 500/3/1$).

Organometallic-mediated radical copolymerization of $\gamma\text{M}\gamma\text{BL}$ and VAc via degenerative chain transfer (DT). $\gamma\text{M}\gamma\text{BL}$ (0.49 g, 5.0 mmol) were degassed by three freeze-pump-thaw cycles and transferred to a 15 mL Schlenk tube with $\text{Co}(\text{acac})_2$ (0.013 g, 0.05 mmol) and V-70 (0.046 g, 0.15 mmol) under argon. Degassed VAc (1.84 mL, 1.72 g, 20 mmol) was injected under argon. The reaction mixture ($f^\circ_{\gamma\text{M}\gamma\text{BL}} = 0.2$, $[\text{VAc}]_0/[\gamma\text{M}\gamma\text{BL}]_0/[\text{V-70}]_0/[\text{Co}(\text{acac})_2]_0 = 400/100/3/1$) was heated at 40 °C for 28 h. Samples were regularly picked out of the tube and added with traces of TEMPO in order to quench the polymerization. The monomer conversion and the molecular parameters (M_n , D) of the polymer were determined by ^1H NMR in CDCl_3 and SEC calibrated with polystyrene in THF, respectively. After 28 h, the polymerization mixture was quenched by addition of 1 mL TEMPO in THF (0.20 g/mL). The final copolymer was purified by precipitation in heptane (three times) and dried overnight under vacuum at 80 °C before characterization via ^1H NMR, ^{13}C NMR, HSQC and COSY in CDCl_3 .

Synthesis of PVAc-*b*-P($\gamma\text{M}\gamma\text{BL-co-VAc}$) block copolymer by OMRP. A solution of alkylcobalt(III) initiator (PVAc- $\text{Co}(\text{acac})_2$) in CH_2Cl_2 (0.23 mL of a 0.111 M stock solution, 0.025 mmol) was added into a 15 mL Schlenk tube followed by evaporation of CH_2Cl_2 under reduced pressure at room temperature. Degassed VAc (1.20 mL, 1.08 g, 12.5 mmol) was injected under argon at 40 °C. After 3 h, a sample was picked out of the tube and added with traces of TEMPO (~10 mg/mL) in order to quench the polymerization for determining the monomer conversion by ^1H NMR in CDCl_3 (conversion = 27 %) and the molecular parameters of the PVAc precursor (10000 g/mol, $D = 1.06$) by $\text{SEC}_{\text{THF cal PS}}$. Then, unreacted VAc was evaporated under reduced pressure at room temperature. The degassed mixture of $\gamma\text{M}\gamma\text{BL}$ (0.25 g, 2.5 mmol) and VAc (0.96

mL, 0.86 g, 10 mmol) were injected under argon. The polymerization medium was heated at 40 °C for 15 h and samples were regularly taken and added with traces of TEMPO in order to quench the polymerization. The monomer conversion and the molecular parameters (M_n , D) of the polymer were determined by ^1H NMR in CDCl_3 and $\text{SEC}_{\text{THF cal PS}}$, respectively. After 15 h, the polymerization mixture was quenched by addition of 1 mL TEMPO in THF (0.20 g/mL) (global $\text{conv} = 59\%$, $M_n \text{ SEC THF cal PS} = 19000 \text{ g/mol}$, $D = 1.43$). The final copolymer was purified by precipitation in n-heptane (three times) and dried overnight under vacuum at 80 °C before characterization via ^1H NMR, ^{13}C NMR, HSQC and COSY in CDCl_3 .

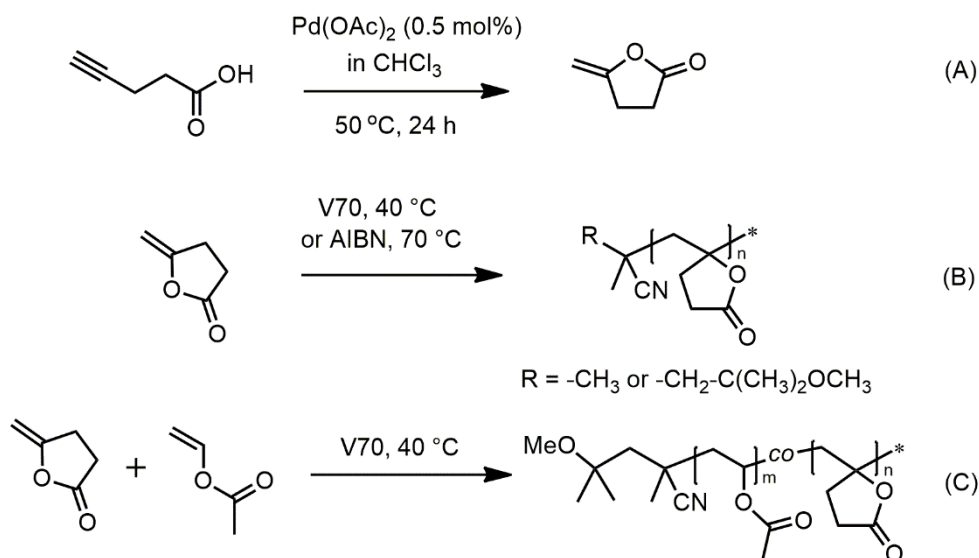
Base hydrolysis of poly($\gamma\text{M}\gamma\text{BL-co-VAc}$). Poly($\gamma\text{M}\gamma\text{BL-co-VAc}$) (1 g, 13800 g/mol, $F_{\gamma\text{M}\gamma\text{BL}} = 0.32$) was dissolved in THF (10 mL). NaOH (1 g, 25 mmol) in deionized water (10 mL) was added to the reaction mixture followed by stirring at room temperature for 48 h. The solution was then dialyzed (membrane 1 kDa) against distilled water for 48 h followed by lyophilisation. The copolymer, recovered as a powder, was characterized via ^1H NMR, ^{13}C NMR, HSQC and COSY in D_2O and by FT-IR.

RESULTS AND DISCUSSION

Synthesis and conventional radical polymerization of $\gamma\text{M}\gamma\text{BL}$.

A straightforward synthesis of methylene lactones consists in the cycloisomerization of γ -alkynoic acids catalyzed by palladium,^{66,67} gold,⁶⁸⁻⁶⁹ copper^{70,71} or cobalt⁷² complexes. Inspired by a recent report,⁶⁷ we prepared the five membered ring $\gamma\text{M}\gamma\text{BL}$ through cycloisomerization of 4-pentyn-1-oic acid using 0.5 mol% of $\text{Pd}(\text{OAc})_2$ as catalyst (Scheme 2A). Compared to the original work,⁶⁷ water was replaced by chloroform as solvent to avoid the hydrolysis of the targeted lactone into 4-

oxo-pentynoic acid. The conversion of 4-pentyn-1-oic acid reached 77 % after 45 h at room temperature but was almost complete after 24 h when performed at 50 °C, as indicated by the ¹H NMR spectrum in Figure S1b. The vinyl lactone was then isolated in a 70 % yield by silica gel chromatography. ¹H and ¹³C NMR spectra (Figure S1c and S1d, respectively) confirmed the structure and the purity of γ M γ BL which was stored under nitrogen at -6 °C before use in polymerization. Note that neither γ M γ BL nor γ -alkynoic acid can be extracted from the biomass.



Scheme 2. Synthesis and conventional radical (co)polymerization of γ M γ BL.

The conventional radical homopolymerization of γ M γ BL was first tested in bulk using a low temperature azo-initiator, namely 2,2'-azobis(4-methoxy-2,4-dimethyl valeronitrile) (V70), at 40 °C (Scheme 2b), but no polymerization occurred under these conditions (Table 1, entry 1). However, the conversion of γ M γ BL reached 41 % when the polymerization was conducted at 70 °C using 5 mol % of azobis(isobutyronitrile) (AIBN) as initiator (Table 1, entry 2). A poly(γ -methylene- γ -butyrolactone) (P γ M γ BL) with a M_n SEC of 4200 g/mol and a dispersity of 1.89 was

obtained. The ^1H NMR (Figure 1a) as well as the COSY and HSQC (Figure S2) experiments confirmed the structure of the $\text{P}\gamma\text{M}\gamma\text{BL}$.

Table 1. Conventional radical (co)polymerization of $\gamma\text{M}\gamma\text{BL}$.

Entry	Initiator / Temp	$f_{\gamma\text{M}\gamma\text{BL}}^{\circ}$	f_{VAc}°	Conv. (%)		M_n^{SEC} (g/mol)	D	$F_{\gamma\text{M}\gamma\text{BL}}$
				$\gamma\text{M}\gamma\text{BL}$	VAc			
1	V70 / 40 °C	1	0	<1 ^a	NA	/	/	/
2	AIBN / 70 °C	1	0	41 ^a	NA	4200 ^c	1.89 ^c	1.00
3	V70 / 40 °C	0.20	0.80	66 ^b	75	12000 ^d	2.24 ^d	0.19 ^e
4	V70 / 40 °C	0.40	0.60	54 ^b	57	8100 ^d	2.01 ^d	0.32 ^e

Conditions: bulk polymerization, 24 h, 5 mol% of azoinitiator vs monomer(s). ^a Determined by gravimetry. ^b Determined by ^1H NMR in CDCl_3 . ^c Determined by $\text{SEC}_{\text{DMF cal PS}}$. ^d Determined by $\text{SEC}_{\text{THF cal PS}}$. ^e Determined by ^1H NMR in CDCl_3 .

Next, we considered the conventional radical copolymerization $\gamma\text{M}\gamma\text{BL}$ with its acyclic analog, i.e. vinyl acetate (Scheme 2c). The $\gamma\text{M}\gamma\text{BL}/\text{VAc}$ copolymerization was carried out in bulk for 24 h at 40 °C in the presence of 5 mol% of V70. Two initial molar fractions of $\gamma\text{M}\gamma\text{BL}$ ($f_{\gamma\text{M}\gamma\text{BL}}^{\circ}$) were considered, i.e. 0.2 and 0.4 (Table 1, entries 3 and 4). In both cases, the comonomer conversion exceeded 50 %. After isolation by precipitation in heptane, polymers were analyzed by ^1H NMR (Figure 1b) but also by COSY and HSQC (Figure S3). The latter confirmed the presence of $\gamma\text{M}\gamma\text{BL}$ and VAc units in both structures. The incorporation of $\gamma\text{M}\gamma\text{BL}$ within the copolymer was quantified by ^1H NMR by comparing the relative intensity of the signal corresponding to the methylene protons **e** of $\gamma\text{M}\gamma\text{BL}$ units at 2.6 ppm and the signal **b** assigned to the methine protons of VAc units around 5 ppm. Accordingly, we found that 19 and 32 mol% of $\gamma\text{M}\gamma\text{BL}$ were respectively incorporated in the $\text{P}(\gamma\text{M}\gamma\text{BL-co-VAc})$ s (Table 1 entries 3 and 4, respectively). Interestingly, the

molar fraction of γ M γ BL in the copolymer ($F_{\gamma\text{M}\gamma\text{BL}}$) was only slightly lower than its molar fraction in the initial feed ($f^{\circ}_{\gamma\text{M}\gamma\text{BL}}$). This observation was further corroborated by the reactivity ratios measured hereafter.

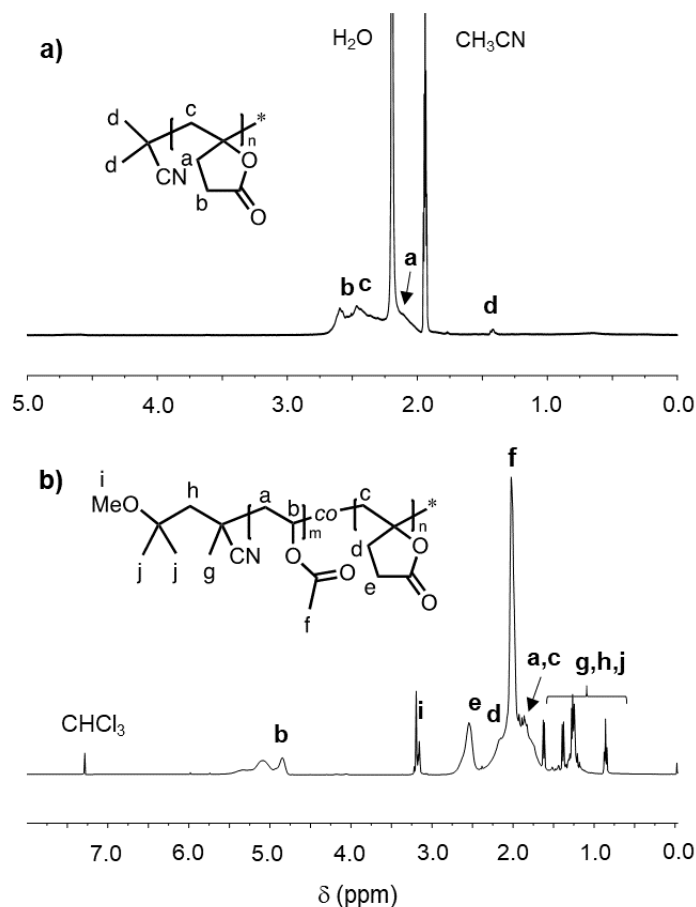


Figure 1. ¹H NMR of P γ M γ BL (a) and P(γ M γ BL-co-VAc) ($F_{\gamma\text{M}\gamma\text{BL}} = 0.32$) (b) in CD₃CN and CDCl₃ respectively.

In order to determine the γ M γ BL/VAc reactivity ratios and get insight into the distribution of the γ M γ BL and VAc units, a series of copolymerizations with different initial feed compositions ($f^{\circ}_{\gamma\text{M}\gamma\text{BL}}$ ranging from 0.1 to 0.7) were initiated by V70 in bulk at 40 °C (Table S1). Polymerizations were stopped at low conversion to prevent significant composition drift. The copolymers were

purified by precipitation in heptane before measuring their composition by ^1H NMR as described above. These experimental data were then used to determine the reactivity ratios by the Fineman-Ross⁶¹ (**FR**, Figure 2a) and Kelen-Tüdös⁶² (**KT**, Figure 2b) linearization methods and by the non-linear least square fitting method based on the Mayo Lewis equation^{63,64} (**NL**, Figure 2c). Note that the reactivity ratios obtained by these methods are highly consistent ($r_{\gamma\text{M}\gamma\text{BL}} = 0.2$, $r_{\text{VAc}} = 1.05$). The low value of $r_{\gamma\text{M}\gamma\text{BL}}$ is in agreement with its low tendency to homopolymerize at 40 °C. On the other hand, the r_{VAc} close to 1 indicates that radical chains with a VAc terminal unit react almost randomly with $\gamma\text{M}\gamma\text{BL}$ and VAc. Based on these reactivity ratio values, we also evaluated the possible composition drift along the P($\gamma\text{M}\gamma\text{BL-co-VAc}$) copolymer using the Skeist's model.⁶⁵ Figure 2d represents the evolution of the cumulative ($F_{\gamma\text{M}\gamma\text{BL}}^{\text{cumul}}$) and instantaneous ($F_{\gamma\text{M}\gamma\text{BL}}^{\text{inst}}$) molar fraction of $\gamma\text{M}\gamma\text{BL}$ in the P($\gamma\text{M}\gamma\text{BL-co-VAc}$) copolymer as a function of the overall molar monomer conversion when using 40 mol% of $\gamma\text{M}\gamma\text{BL}$ in the initial feed ($f_{\gamma\text{M}\gamma\text{BL}}^{\text{c}} = 0.4$). As a confirmation of the validity of this model, the cumulative composition of the P($\gamma\text{M}\gamma\text{BL-co-VAc}$) copolymer ($F_{\gamma\text{M}\gamma\text{BL}} = 0.32$) formed at 54 % of overall conversion (Table 1, entry 4) is in agreement with the cumulative molar fraction of $\gamma\text{M}\gamma\text{BL}$ predicted at this conversion by the Skeist's model (see Figure 2d, $F_{\gamma\text{M}\gamma\text{BL}}^{\text{cumul}} = 0.33$). Interestingly, the instantaneous composition ($F_{\gamma\text{M}\gamma\text{BL}}^{\text{inst}}$) remains relatively constant at least until 60 % conversion and suggests a low drift of the composition along the polymerization. At higher conversion, the Skeist's curve indicates a significant increase of the $\gamma\text{M}\gamma\text{BL}$ content in the copolymer. Nevertheless, one must keep in mind that incorporating more than 50 % of this monomer within the copolymer is difficult given its low propensity to homopolymerize. The knowledge of the insertion mode of the comonomers within P($\gamma\text{M}\gamma\text{BL-co-VAc}$) copolymers is a major asset for addressing their precision synthesis via reversible deactivation radical polymerization.

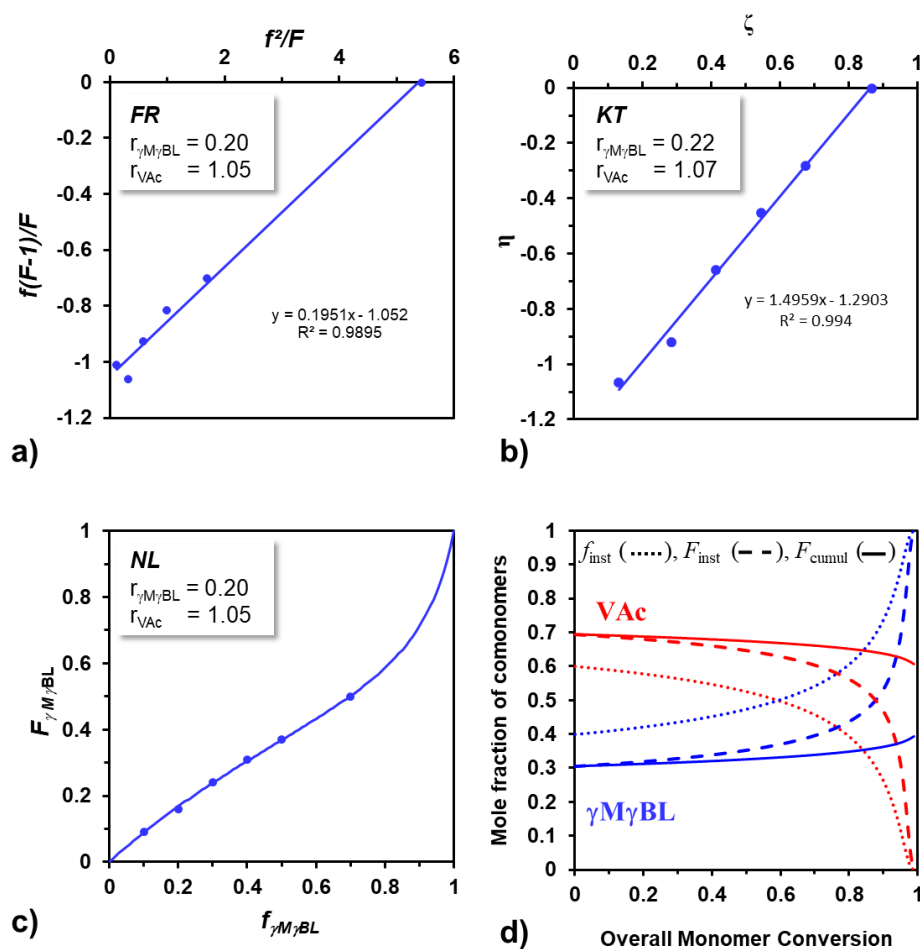
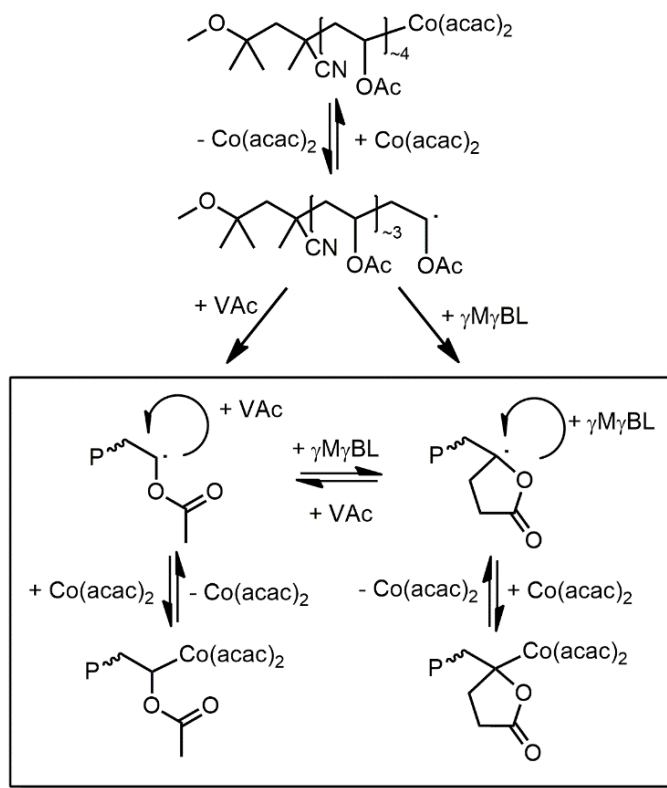


Figure 2. Determination of the reactivity ratios for the radical copolymerization of $\gamma\text{M}\gamma\text{BL}$ and VAc in bulk at 40 °C by three methods: Fineman-Ross (a), Kelen-Tüdös (b) and the non-linear least square fitting method based on the Mayo Lewis equation (c). Experimental data are presented in Table S1. (d) Evolution of the instantaneous molar fraction in the feed ($f_{\gamma\text{M}\gamma\text{BL}}$) but also of the cumulative ($F_{\gamma\text{M}\gamma\text{BL}}$) and instantaneous ($F_{\text{inst } \gamma\text{M}\gamma\text{BL}}$) molar fraction of the comonomers in the copolymer with the overall molar monomer conversion for an initial $\gamma\text{M}\gamma\text{BL}$ feed ratio of 0.4 ($f_{\gamma\text{M}\gamma\text{BL}}^0$). Compositions are calculated based on Skeist's model.

Reversible deactivation radical (co)polymerization of γ M γ BL.

As a reminder, high level of control was achieved for the OMRP of VAc, the acyclic analog of γ M γ BL, when Co(acac)₂ was used as controlling agent.^{43,44} The equilibrium between the alkylcobalt(III) dormant species and the active radical species occurred via reversible cleavage of the Co-C bond at moderate temperature. Typically, the polymerization of VAc proceeded in a controlled manner when carried out in bulk at 40 °C using a preformed PVAc_{~4}-Co(acac)₂ species as initiator (Scheme 3). Under these conditions, PVAc with low dispersity ($D \sim 1.1$) and predictable molar mass was formed.⁴⁴ Considering the structural similarities between VAc and γ M γ BL, the homopolymerization of the vinyl lactone was tested first under the same conditions, namely 40 °C, in bulk, with PVAc_{~4}-Co(acac)₂ species as initiator [γ M γ BL]/[PVAc_{~4}-Co(acac)₂] = 500 (Table S2, entry 1). However, the polymerization stopped after 6 h (conversion = 9 %) and no evolution of the molar mass was observed along the polymerization ($M_{n \text{ SEC}} \sim 7000$ g/mol, $D \sim 1.6-1.7$), suggesting an uncontrolled process. Note that very similar results were obtained when repeating the same experiment at 65 °C (Table S2, entry 2). Such a low tendency of γ M γ BL to propagate via OMRP most probably results from premature irreversible termination reactions.



Scheme 3. Organometallic-mediated radical copolymerization of $\gamma\text{M}\gamma\text{BL}$ and VAc.

In order to gain insight in the OMRP of $\gamma\text{M}\gamma\text{BL}$ and to prepare novel polymer structures, we considered the reversible deactivation radical copolymerization of $\gamma\text{M}\gamma\text{BL}$ and VAc (Scheme 3). A series of organometallic-mediated radical copolymerizations of $\gamma\text{M}\gamma\text{BL}$ and VAc was first carried out in bulk at 40 °C with the $\text{PVAc}_{\sim 4}\text{-Co}(\text{acac})_2$ initiator (Table 2). Three initial composition feeds were considered with $\gamma\text{M}\gamma\text{BL}$ molar fraction ($f^{\circ}_{\gamma\text{M}\gamma\text{BL}}$) ranging from 0.2 to 0.7. Molecular parameters (M_n and D) of the copolymer and the monomer conversion were monitored throughout the polymerization via SEC and ^1H NMR, respectively. At the desired time/conversion, TEMPO was added to the reaction medium in order to trap irreversibly the radical chains and stop the polymerization. The content of $\gamma\text{M}\gamma\text{BL}$ in the final copolymer ($F_{\gamma\text{M}\gamma\text{BL}}$), measured by ^1H NMR, is

indicated in Table 2. A representative spectrum is provided in Figure S4a. The structure of the P(γ M γ BL-*co*-VAc) copolymer is also confirmed by the COSY and HSQC spectra (Figures S4b and S4c).

Regardless of the initial composition feed, PVAc-*4*-Co(acac)₂ successfully initiated the γ M γ BL/VAc copolymerization at 40 °C. Moreover, the copolymerization rate was clearly lower when the content of γ M γ BL in the feed was higher. After 12 h, the conversion reached 36 %, 20 % and 11 % for $f_{\gamma\text{M}\gamma\text{BL}}^0$ equal to 0.2, 0.4 and 0.7, respectively (Table 2). This trend is obvious when considering the time dependence of the $\ln[M]_0/[M]$ function (Figure 3a) for the three compositions. The molar fraction of γ M γ BL was systematically lower in the copolymer compared to the feed as suggested by the reactivity ratios ($r_{\gamma\text{M}\gamma\text{BL}} = 0.2$, $r_{\text{VAc}} = 1.05$). Note that the experimental $F_{\gamma\text{M}\gamma\text{BL}}$ ($F_{\gamma\text{M}\gamma\text{BL exp}} = 0.19, 0.33$ and 0.53) were close to the prediction based on these reactivity ratios ($F_{\gamma\text{M}\gamma\text{BL th}} = 0.17, 0.31$ and 0.50). As an additional proof of the incorporation of γ M γ BL in the copolymers, the thermal degradation profile of the copolymers and their glass transition temperature (T_g) differ from those of PVAc (Figure S5). Due to the incorporation of rigid lactones along the backbone of the P(γ M γ BL-*co*-VAc) copolymers, T_g increased from 31 °C for a homo-PVAc prepared by OMRP to 64 °C, 77 °C and 83 °C for copolymers with $F_{\gamma\text{M}\gamma\text{BL}}$ equal to 0.19, 0.33 and 0.53, respectively.

Table 2. Organometallic-mediated radical (co)polymerization of γ M γ BL and VAc.

Entry	$f_{\gamma\text{M}\gamma\text{BL}}^{\circ}$	f_{VAc}°	Time (h)	Conv (%) ^a	$M_{n \text{ SEC}}$ (g/mol) ^b	\mathcal{D}^b	$F_{\gamma\text{M}\gamma\text{BL}}^a$	$M_{n \text{ th}}$ (g/mol) ^d
1	0.20	0.80	2	7	5200	1.10		
			4	15	6600	1.17		
			6	21	7900	1.22		
			8	27	8500	1.28		
			10	32	9400	1.32		
			12	36	10200	1.33	0.19	15900
2	0.40	0.60	3	6	4000	1.13		
			6	11	5700	1.16		
			9	15	6900	1.22		
			12	20	8000	1.28		
			15	25	8400	1.36		
			30	35	12000	1.56	0.33	15800
3	0.70	0.30	3	4	4400	1.19		
			6	6	5900	1.25		
			9	9	6900	1.36		
			12	11	7900	1.43		
			30	20	9500 ^c	1.63 ^c	0.53	9200

Conditions: 40 °C, [monomer]/[RCo] =500. ^a Total monomer conversion determined by ¹H NMR in CDCl₃.

^b Determined by SEC in THF using a PS calibration, ^c Determined by SEC in DMF/LiBr using a PS calibration due to the low solubility of this sample in THF. ^d Theoretical molar mass ($M_{n \text{ th}}$) calculated based on the [monomer]/[RCo] ratio, the conversion and the composition of the copolymer.

As illustrated in Figure 3b, M_n of P(γ M γ BL-*co*-VAc) regularly increases with monomer conversion, suggesting the controlled character of the copolymerization. The shift of the SEC chromatograms of the samples withdrawn at different polymerization times is represented in Figure 3c. Moreover, the dispersities remained low ($\mathcal{D} \sim 1.1$ -1.3) until 30 % conversion but tended to broaden at higher

conversion, especially for the γ M γ BL-rich copolymers. The theoretical molar masses of the final copolymers are also mentioned in Table 2. The latter are calculated based on the monomer/initiator ratio, the conversion and the composition of the copolymers. Note that $M_{n\text{ exp}}$ is determined by SEC using a PS calibration which might also account for the deviation from $M_{n\text{ th}}$. As expected for a controlled process, the P(γ M γ BL-co-VAc) molar mass also strongly depends on the comonomer/initiator ratios. For a similar γ M γ BL/VAc molar ratio (2/8), P(γ M γ BL-co-VAc) with higher molar masses were obtained when increasing the [comonomers]/[PVAc-Co] ratio as illustrated in Figure S6 and Table S3.

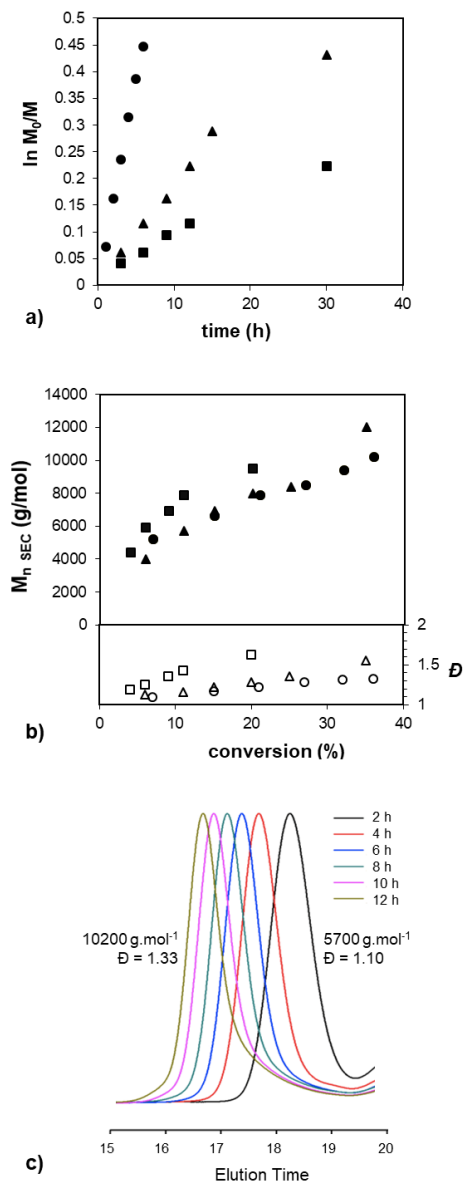


Figure 3. (a) Time dependence of $\ln[M]_0/[M]$ and (b) dependence of M_n (full symbols) and \bar{D} (hollow symbols) on the total monomer conversion for the OMRP of $\gamma M \gamma BL$ and VAc with different compositions : $f_{\gamma M \gamma BL}^0 = 0.2$ (●), 0.4 (▲) and 0.7 (■) (see Table 2 for detailed conditions). (c) Overlay of SEC traces for the OMRP of $\gamma M \gamma BL$ and VAc ($f_{\gamma M \gamma BL}^0 = 0.2$, Table 2 entry 1).

Next, we took advantage of the controlled copolymerization of γ M γ BL and VAc for macromolecular engineering, in particular for the one-pot synthesis of PVAc-*b*-P(γ M γ BL-*co*-VAc) block copolymers. The general strategy consists in the sequential OMRP of VAc and γ M γ BL/VAc copolymerization (Figure 4). In practice, a well-defined PVAc-Co(acac)₂ precursor (M_n SEC = 10000 g/mol, $D = 1.06$) prepared at 40 °C in bulk from PVAc₄-Co(acac)₂ served as macroinitiator for the γ M γ BL/VAc copolymerization ($f^\circ\gamma$ M γ BL = 0.2) performed under the same experimental conditions. The overlay of the SEC chromatograms in Figure 4 confirms the efficiency of the chain extension as well as the controlled character of the synthesis of the statistical sequence. Indeed, the chromatogram corresponding to the PVAc macroinitiator was clearly shifted towards higher molar masses. It should be noted, however, that a tailing appeared on the low molar mass side of the peak probably due to bimolecular radical termination or chain transfer reactions causing a broadening of the peaks beyond 30 % of monomer conversion. At this stage, we cannot exclude that the broadening of the SEC peaks also results from difficulty to reactivate some inverted head-to-head γ M γ BL adducts. Nevertheless, γ M γ BL-containing block copolymers were successfully prepared for the first time.

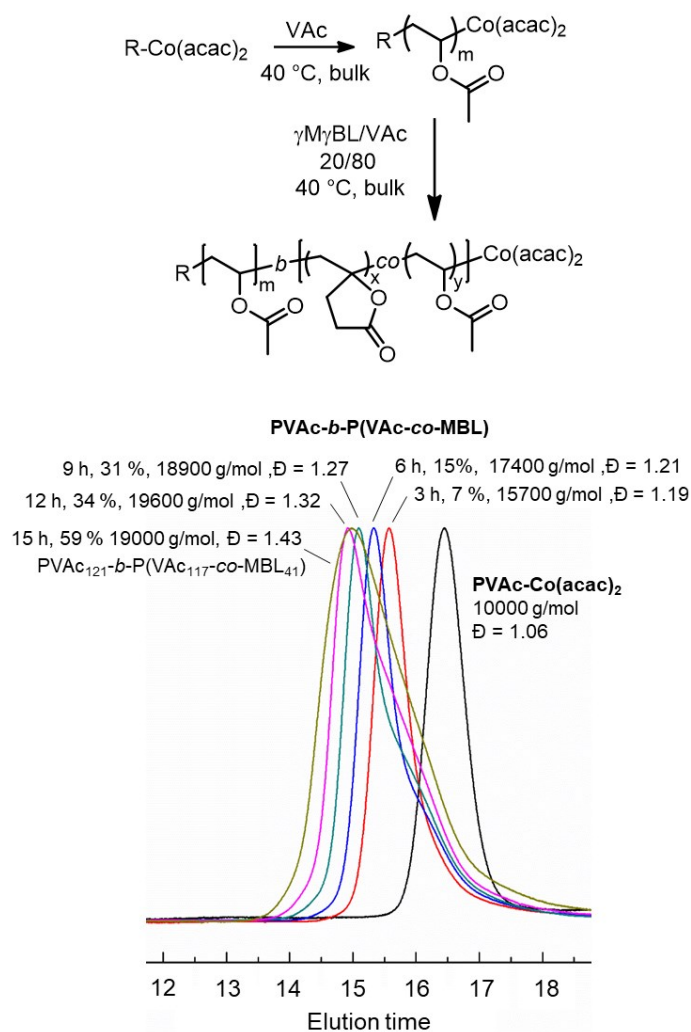


Figure 4. General strategy for the synthesis of $\gamma M\gamma BL$ -containing block copolymers by OMRP and overlay of the SEC chromatograms for the homoPVAc-Co(acac)₂ precursor and the resulting PVAc-*b*-P($\gamma M\gamma BL$ -co-VAc) diblocks.

Some interesting mechanistic conclusions can be drawn at this stage on the OMRP of $\gamma M\gamma BL$. All the above mentioned experiments were initiated with a preformed alkylcobalt(III) species in the absence of additional radical source and therefore necessarily followed a reversible termination

(RT) pathway,^{43,73,74} which consists in the reversible homolytic rupture of the cobalt-carbon bond at the polymer chain-end (Figure 5). In the case of the OMRP of VAc, the bond dissociation enthalpy of the PVAc-Co(acac)₂ model (species **2**) was estimated at 9.2 Kcal/mol by DFT calculations. Moreover, in absence of coordinating molecules, the PVAc-Co(acac)₂ dormant species also benefits from extra-stabilization of 3.9 Kcal/mol upon intramolecular chelation via the terminal ester unit of the PVAc chain (species **3**).^{43,73,74} For the sake of the comparison, we performed similar DFT calculations for γ M γ BL. The bond dissociation enthalpy of the model P γ M γ BL-Co(acac)₂ (species **2'**) was slightly higher compared to the PVAc-Co(acac)₂ one, namely 12.0 Kcal/mol. However, the stabilization of the dormant P γ M γ BL-Co(acac)₂ by intramolecular chelation of the cobalt by the ester function unit is hampered by the geometrical constraint of the lactone. The reorganization of the coordination sphere from square pyramidal with apical alkyl group to square pyramidal with the apical position occupied by one O atom of one acac ligand, which is required to generate a *cis* vacant site for monomer chelation in species **3'**, is energetically costly (+15.1 kcal/mol), but cannot be compensated by donation of the carbonyl oxygen electron density as in species **3**. Instead, only a slight interaction with the endocyclic oxygen atom may occur, as shown by the distortion imposed on the cobalt-bonded C atom configuration (Co-C-O = 84.1°; Co-C-C(H₃) = 117.1°; Co-C-C(H₂) = 117.6°). This interaction, however, is very weak (Co...O = 2.27 Å; cf. with the Co-O distance of 1.93 Å in the chelated VAc monomer in species **3**). Overall, the chelated PVAc-Co and non-chelated P γ M γ BL-Co (dormant species **3** and **2'**, respectively) exhibit quite similar global bond dissociation enthalpies (13.1 and 12.0 Kcal/mol, respectively) and should efficiently reactivate under similar conditions, for example in bulk at 40 °C. Consequently, the extremely low conversion reported earlier for the homopolymerization of γ M γ BL by OMRP at 40 °C cannot result from a high P γ M γ BL-Co(acac)₂ bond strength. It can

rather be attributed to a low k_p of $\gamma M\gamma BL$ at this temperature. As a confirmation, no conversion was observed for the conventional radical homopolymerization of $\gamma M\gamma BL$ at 40 °C (Table 1, entry 1). Concerning the OMRP of $\gamma M\gamma BL$ at 70 °C, it is reasonable to assume that the $P\gamma M\gamma BL-Co(acac)_2$ bond is too weak to establish an appropriate equilibrium between dormant and active species at this temperature, leading to massive and premature termination of the radical chains and ultimately inhibition of the polymerization by accumulation of the cobalt(II) deactivator in the polymerization medium. However, the successful organometallic-mediated radical copolymerization of VAc and $\gamma M\gamma BL$ at 40 °C is fully consistent with similar C-Co bond strength for the VAc and $\gamma M\gamma BL$ model dormant species. Under these conditions, both dormant species can reactivate and the terminal $\gamma M\gamma BL$ radicals can further cross propagate with VAc leading to well-defined $P(\gamma M\gamma BL-co-VAc)$ copolymers.

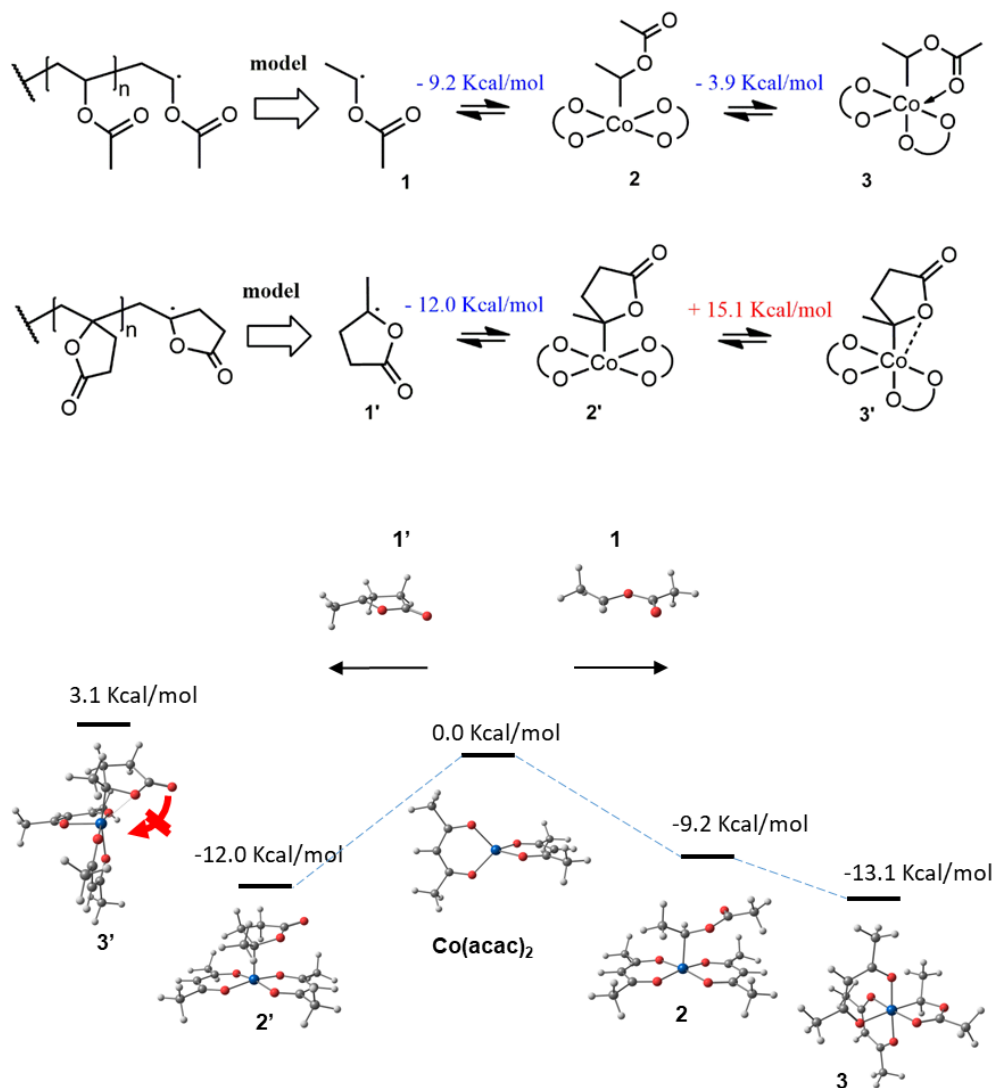
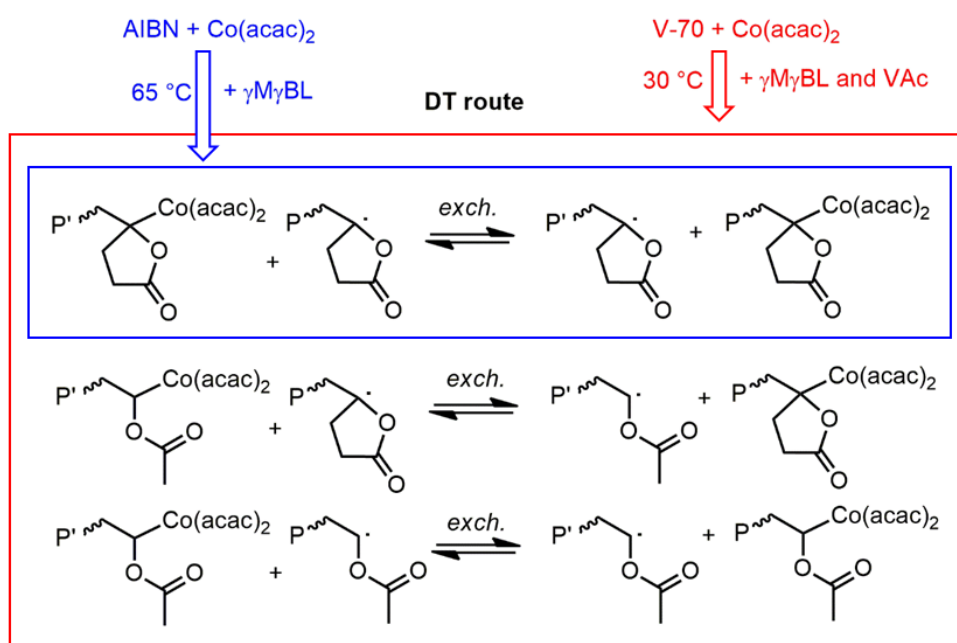


Figure 5. DFT calculation of the bond dissociation enthalpies for the γ M γ BL-Co(acac)₂ and VAc-Co(acac)₂ model species.

In addition to the reversible termination (RT) pathway, OMRP is also known to proceed via a degenerative chain transfer (DT) mechanism, in which an active radical chain displaces the dormant chain bound to the metal via an associative exchange reaction.^{43,73,74} This mode notably prevails in the absence of coordinating molecules and when an excess of radicals relative to cobalt

is generated in the polymerization medium. In this case, the polymerization rate and radical concentration are close to those observed for conventional radical polymerizations. In practice, the DT polymerizations are initiated from commercially available conventional radical initiators used in excess compared to the cobalt complex, preventing the synthesis of sensitive alkylcobalt(III) initiators. Both the homopolymerization of γ M γ BL and the γ M γ BL/VAc copolymerization were tested in the DT mode (scheme 4).



Scheme 4. Mechanism of the homopolymerization of γ M γ BL and the γ M γ BL/VAc copolymerization via OMRP in the DT mode.

In practice, the polymerization of γ M γ BL was performed in bulk in the presence of Co(acac)₂ and AIBN ($[\gamma\text{M}\gamma\text{BL}]_0/[\text{AIBN}]_0/[\text{Co}(\text{acac})_2]_0 = 500/3/1$) at 65 °C in order to ensure the formation of P γ M γ BL (Table S4, entry 1). Under these conditions, the conversion increased from 6 to 28 %

between 3 h and 24 h of reaction without significant evolution of the polymer molar mass ($M_n \sim 7000$ g/mol, $D \sim 1.6-1.8$), indicating an uncontrolled polymerization process. On the other hand, inspired by previous reports on the OMRP of VAc by DT, the controlled copolymerization of γ M γ BL/VAc (f°_{γ M γ BL = 0.2) was examined in the DT regime at 30 °C using three equivalents of V70 relative to Co(acac)₂ (Table S4, entry 2). Kinetics data and the molecular parameters (M_n , D) dependence on the monomer conversion are plotted in Figure 6. In contrast to the γ M γ BL/VAc copolymerization initiated with the PVAc-Co(acac)₂ initiator and carried out under the RT regime, an induction period of several hours was observed in the DT mode (Figure 6b). As described elsewhere for the OMRP of VAc,⁴³ the induction period corresponds to the time necessary to generate a sufficient amount of radicals for converting most of the Co^{II}(acac)₂ into the alkyl-cobalt(III) dormant species. After this period, a controlled polymerization of γ M γ BL and VAc was observed as suggested by the pseudo-first order kinetics and the linear increase of the molar mass with the monomer conversion (Figure 6b) while maintaining a low dispersity ($D \sim 1.1-1.3$) (Figure 6a). Overall, this approach represents a straightforward route for the controlled synthesis of P(γ M γ BL-co-VAc)s involving readily available initiator and controlling agent.

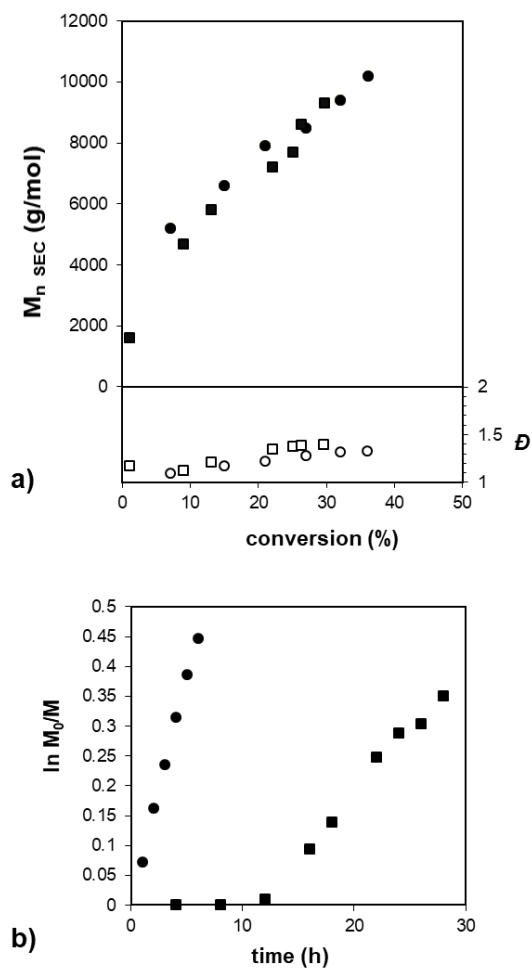
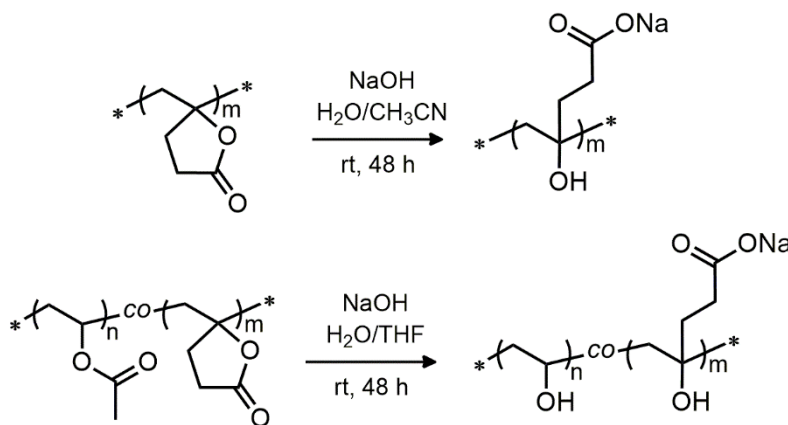


Figure 6. (a) Time dependence of $\ln[M]_0/[M]$ and (b) dependence of M_n and D on the monomer conversion for the OMRP of γ M γ BL and VAc via reversible termination (RT) (●) or degenerative chain transfer (DT) (■). Conditions: (●) $[VAc]_0/[\gamma M \gamma BL]_0/[PVAc_4-Co(acac)_2]_0 = 400/100/1$, 40 °C, (■) $[VAc]_0/[\gamma M \gamma BL]_0/[V70]_0/[Co(acac)_2]_0 = 400/100/3/1$, 30 °C.

Post-polymerization modification of γ M γ BL-based (co)polymers.

Poly(vinyl alcohol) (PVA) is a major industrial polymer commonly prepared by hydrolysis of poly(vinyl acetate).⁷⁵⁻⁷⁷ The presence of one hydroxyl group per repeating unit makes it highly

hydrophilic although PVA with high level of hydrolysis exhibit limited water solubility due to the formation of regular hydrogen-bonding networks.^{45,75,78,79} On the other hand, the literature is replete with examples of modified-PVA produced by radical copolymerization of VAc with comonomers prior to hydrolysis or partial hydrolysis.^{77,80–83} Both approaches disrupt the regular sequence of hydroxyl groups typical of PVA. In this respect, the hydrolysis of the γ M γ BL-containing (co)polymers prepared above should offer new functionalities to PVA without altering its characteristic hydroxyl sequence. Indeed, the hydrolysis of the pendant lactone ring should release one alcohol moiety and one carboxylic acid group within the same repeating unit (scheme 5). This equals to the modification of the PVA backbone at the methine position. Interestingly, decorating PVAs with carboxylic acid moieties should impart to them unique pH-responsiveness. These were strong incentives to investigate the hydrolysis of both P γ M γ BL and P(γ M γ BL-*co*-VAc) and to carry out a preliminary study of its water solution properties.



Scheme 5. Hydrolysis of P γ M γ BL and P(γ M γ BL-*co*-VAc).

A homo-P γ M γ BL (4200 g/mol, $D = 1.89$) and a P(γ M γ BL-*co*-VAc) (13800 g/mol, $D = 1.65$, $F_{\gamma\text{M}\gamma\text{BL}} = 0.32$), prepared by conventional radical polymerization and OMRP respectively, were subjected to basic hydrolysis. Typically, P γ M γ BL was treated with sodium hydroxide in an acetonitrile/water

(1/1 : v/v) mixture at room temperature for 48 h followed by dialysis against distilled water. Note that the water solubility of the treated polymer was a first indication of significant modification of the polymer structure. The successful hydrolysis of most of the pendant lactone ring of P γ M γ BL was further confirmed by IR (Figure S7b). Indeed, the IR spectrum shows a significant decrease of the characteristic signals of the esters units (C=O ester) at 1759 cm⁻¹ and the appearance of a large band at 3300 cm⁻¹, typical of the hydroxyl moieties, as well as an intense peak at 1556 cm⁻¹ assigned to the carboxylate groups. The ¹H NMR in D₂O of the treated P γ M γ BL, namely the poly(4-hydroxypent-4-enoic acid) (HPPEA), also supports the successful hydrolysis of lactones (Figure 7a). Indeed, a signal corresponding to methylene protons **b** at the alpha position of the carboxyl group appeared at 2.20 ppm. Note that some residual lactone (10 %) was detected at 2.65 ppm. The structure of the hydrolyzed P γ M γ BL was also corroborated by COSY and HSQC (Figure S8). The P(γ M γ BL-*co*-VAc) copolymer (13800 g/mol, $D = 1.65$, $F_{\gamma M \gamma BL} = 0.32$) was treated with sodium hydroxide in a THF/water (1/1 : v/v) mixture at room temperature for 48 h, leading to the corresponding modified PVA copolymer via hydrolysis of both lactones and acyclic pendant esters as confirmed by IR (Figure S7d) and ¹H NMR (Figure 7b). In addition to the peak at 2.20 ppm corresponding to the methylene protons **e**, namely the alpha position of the carboxyl group in the hydrolyzed γ M γ BL units, we also observed characteristic signals of the vinyl alcohol units, namely the methine protons **b** around 4 ppm. In this case, 3 % of unmodified lactone was detected at 2.65 ppm. COSY and HSQC spectra of the P(HPPEA-*co*-VA) copolymer is provided as supporting information (Figure S9).

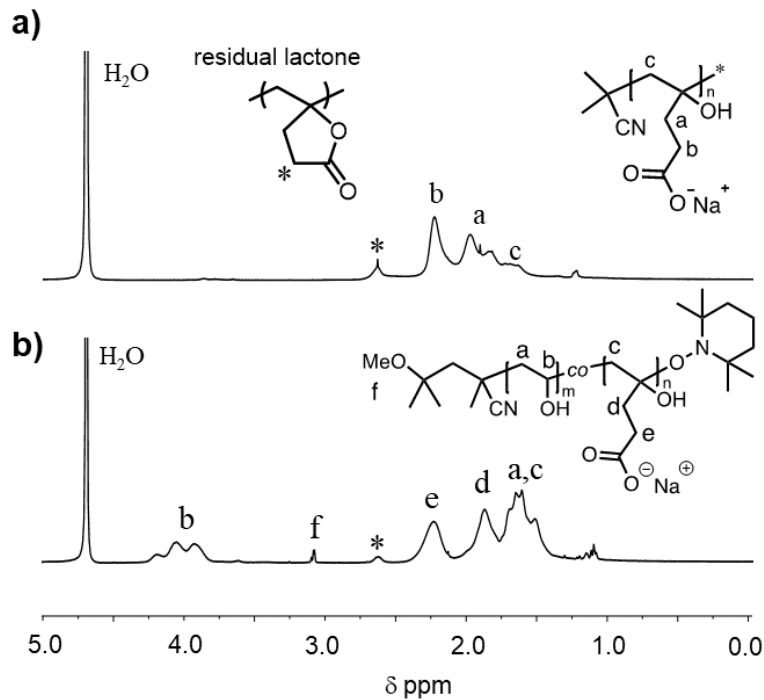


Figure 7. ¹H NMR spectra in D₂O after hydrolysis of (a) PHPEA and (b) P(HPEA-co-VA) obtained by hydrolysis of P γ M γ BL (4200 g/mol, $D = 1.89$) and a P(γ M γ BL-co-VAc) (13800 g/mol, $D = 1.65$, $F_{\gamma\text{M}\gamma\text{BL}} = 0.32$), respectively.

Finally, we carried out a preliminary study of the aqueous solution properties of the PHPEA and P(HPEA-co-VA) ($F_{\text{HPEA}} = 0.32$) (co)polymers prepared above. Given the presence of carboxylic group along their backbone, special care was devoted to their possible pH-responsiveness. As illustrated in Figure 8, both PHPEA and P(HPEA-co-VA) were fully soluble in water at pH 7 (at 5 mg/mL). Under these conditions, the pendant carboxylic acid groups are deprotonated, which favors the (co)polymer solubilization. However, drastic changes occurred upon acidification of the solution to pH 1. Indeed, the PHPEA clearly precipitates after protonation of its carboxylic acid groups leading to the formation of rather large particles as emphasized by DLS (mean diam > 2 μm). In contrast, the aqueous solution of P(HPEA-co-VA) did not turn opaque when acidified to

pH 1, rather it became slightly turbid suggesting the formation of smaller objects. In addition to few large aggregates, DLS emphasized the formation of objects with an average diameter of 550 nm. Compared to PHPEA, which exhibits one pH sensitive carboxylic acid function per repeating unit, the P(HPEA-*co*-VA) presents higher hydroxyl/carboxylic acid molar ratio which favored the stabilization of the submicron objects at low pH. Note that the transition occurred around pH 2.2 and was fully reversible for more than 7 acidification/basification cycles as illustrated in Figure S10.

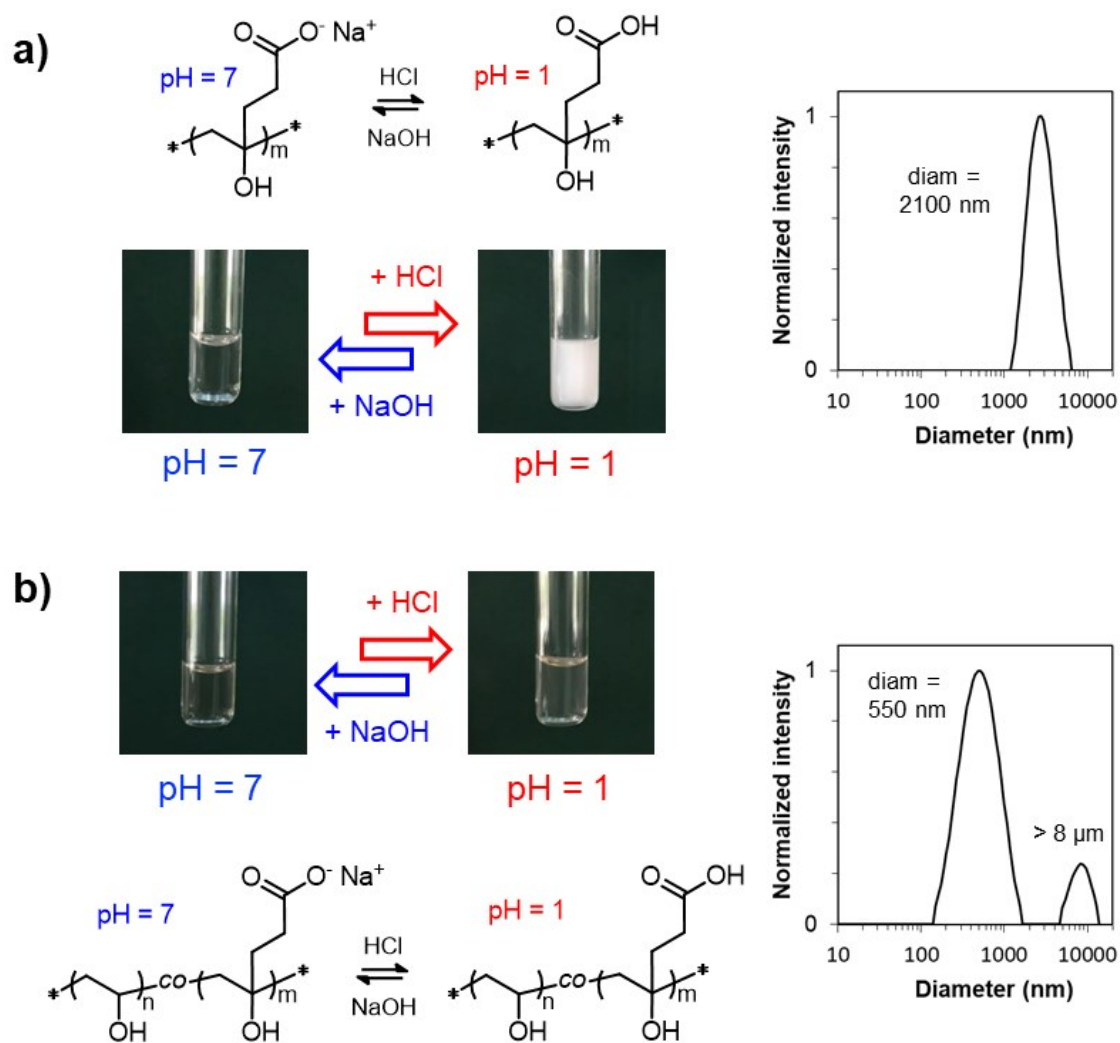


Figure 8. Illustration of the aqueous solution behavior and pH-responsiveness of (a) PHPEA and (b) P(HPEA-*co*-VA) at r.t. at 5 mg/mL .

CONCLUSION

The use of non-conjugated lactones in conventional and reversible deactivation radical polymerizations has previously been largely overlooked so far. In this report, we have shown the

potential of γ M γ BL as monomer and comonomer in combination with vinyl acetate in radical polymerization processes.

Poly(γ M γ BL) was successfully produced by conventional radical polymerization of γ M γ BL at 70 °C, whereas no polymer formed at 40 °C because of a low propagation rate constant under these conditions. However, attempts to polymerize γ M γ BL via OMRP based on Co(acac)₂ failed. This results from the difficulty to find a temperature window which guarantees a sufficient propagation rate constant and ensures a proper equilibrium between active and dormant species, limiting irreversible termination reactions.

In contrast, the conventional radical copolymerization of γ M γ BL and VAc, its acyclic analog, proceeded well at 40 °C. This paved the way to their controlled Co(acac)₂-mediated radical copolymerization, following a reversible termination pathway, at this temperature using a preformed alkyl-cobalt(III) initiator. A series of P(γ M γ BL-co-VAc) with specific molar masses, low and moderate dispersities (\mathcal{D} ~1.2-1.4) and various compositions were produced accordingly. The reactivity ratios were measured by three methods, *i.e.* Fineman-Ross, Kelen-Tüdős as well as the nonlinear approach leading to similar values, *i.e.* $r_{\gamma\text{M}\gamma\text{BL}} = 0.20$, $r_{\text{VAc}} = 1.05$. These numbers confirmed the low propensity of γ M γ BL to self-propagate at 40 °C and the possibility to copolymerize it with VAc. The distribution of γ M γ BL along the copolymer chains was also evaluated by the Skeist model revealing a rather homogeneous incorporation of the vinyl lactone in the copolymer at least until 60 % conversion. DFT calculations confirmed that the model dormant species, namely $\gamma\text{M}\gamma\text{BL-Co(acac)}_2$ and VAc-Co(acac)_2 , have quite similar bond dissociation enthalpy which limits the accumulation of one or the other dormant form in the polymerization medium and favors a controlled process. Interestingly, the controlled

copolymerization of γ M γ BL and VAc was also achieved via degenerative chain transfer mechanism starting from commercially available compounds, i.e. V70 and Co(acac)₂. In addition to controlling the overall composition and the comonomer sequence of the copolymers, mediating the γ M γ BL/VAc radical copolymerization opens several macromolecular engineering opportunities as emphasized by the synthesis of PVAc-*b*-P(γ M γ BL-*co*-VAc) diblock copolymers.

Last but not least, P γ M γ BL and P(γ M γ BL-*co*-VAc) were converted into poly(4-hydroxypent-4-enoic acid) (PHPEA) and P(HPEA-*co*-VA), respectively, via ester hydrolysis under basic conditions. The γ M γ BL units have the particularity to generate one alcohol moiety and one carboxylic acid group on the same chain C atom, giving access to unprecedented carboxylic acid-functionalized poly(vinyl alcohol) without alteration of its characteristic hydroxyl sequence. The pH-responsiveness of both (PHPEA) and P(HPEA-*co*-VA) in water was also demonstrated.

All these results support our initial idea that non-conjugated lactones like γ M γ BL are promising building blocks for the macromolecular engineering based on LAMs and for the design of unique functional and responsive materials.

ACKNOWLEDGMENTS

The authors from Liege thank the Fonds de la Recherche Scientifique (FNRS) and the Fonds Wetenschappelijk Onderzoek – Vlaanderen (FWO) for funding the EOS project n°O019618F (ID EOS: 30902231) and the NECOPOL project (convention U.N054.17). A.D. and C.D. are Research Associate and Research Director by F.R.S.-FNRS, respectively. We are grateful to the CALMIP mesocenter of the University of Toulouse for the allocation of computational resources.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website. Additional data, DFT calculations as well as SEC, NMR, DSC and TGA characterizations.

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