

# Merging CO<sub>2</sub>-Based Building Blocks with Cobalt-Mediated Radical Polymerisation for the Synthesis of Functional Poly(vinyl alcohol)s

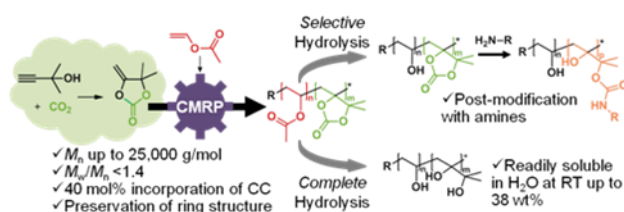
Philip B. V. Scholten,<sup>1,2</sup> Jérémy Demarteau,<sup>1</sup> Sandro Gennen,<sup>1</sup> Julien De Winter,<sup>3</sup> Bruno Grignard,<sup>1</sup> Antoine Debuigne,<sup>1</sup> Michael A. R. Meier,<sup>2</sup> Christophe Detrembleur\*<sup>1</sup>

<sup>1</sup> P.B.V. Scholten, J. Demarteau, Dr. B. Grignard, Dr. A. Debuigne, Dr. C. Detrembleur; Center for Education and Research on Macromolecules (CERM), CESAM Research Unit, University of Liège, Department of Chemistry, Sart-Tilman B6a, 4000 Liège, Belgium; email: christophe.detrembleur@uliege.be

<sup>2</sup> P.B.V. Scholten, Prof. Dr. M.A.R. Meier; Karlsruhe Institute of Technology (KIT), Institute of Organic Chemistry (IOC), Materialwissenschaftliches Zentrum MZE, Straße am Forum 7, 76131 Karlsruhe (Germany)

<sup>3</sup> Dr. Julien De Winter, Organic Synthesis and Mass Spectrometry Laboratory (S2MOS), University of Mons, 23 Place du Parc, B-7000, Mons, Belgium

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## Abstract

The use of CO<sub>2</sub>-based  $\alpha$ -alkylidene cyclic carbonates in controlled radical polymerisation has so far not been exploited, despite the fact that the cyclic carbonate ring offers a multitude of possible modifications. Herein, the synthesis of well-defined copolymers of vinyl acetate (VAc) and 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (DMMDO) using cobalt-mediated radical polymerisation (CMRP) at 40 °C is reported. The controlled nature of the polymerisation was confirmed while molecular weights of up to 25,000 g.mol<sup>-1</sup> and narrow dispersities (< 1.4) were obtained. The copolymer structure was elucidated combining NMR, FT-IR and MALDI-TOF analyses and consists of a polymer backbone with pendant carbonate rings. Further insights into the copolymer structure were gained through the monomers' reactivity ratios and a homogeneous distribution of the DMMDO monomer along the polymer chain was observed. A highly water soluble poly(vinyl alcohol)-based copolymer was obtained by basic hydrolysis, whereas the chemo-selective acidic hydrolysis of the acetate groups left the cyclic carbonate rings untouched, which were then exploited for further post-modification with amines. The precise copolymerisation of VAc with CO<sub>2</sub>-sourced five-membered cyclic carbonate bearing an exomethylene moiety is therefore a powerful tool for the synthesis of new variants of poly(vinyl alcohol)-based copolymers.

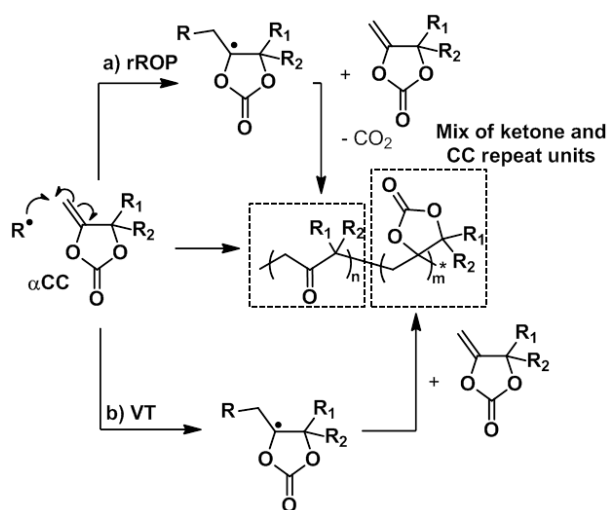
**Keywords:** cobalt-mediated radical polymerisation, vinyl acetate, poly(vinyl alcohol), cyclic carbonate

## Introduction

CO<sub>2</sub> is a very versatile and powerful C1-synthon, which has been extensively used in recent years in light of the valorisation of renewable resources. Five-membered cyclic carbonates (CCs) have emerged as one of the most widely investigated CO<sub>2</sub>-based molecules<sup>1-9</sup> as they are known for their broad reactivity and have found numerous recent applications, such as precursors to chiral building blocks<sup>10-13</sup> and monomers for non-isocyanate poly(urethane)s (NIPUs)<sup>14-18</sup> to only cite a few.

Recently, the (organo)catalysed synthesis of a library of  $\alpha$ -alkylidene cyclic carbonates ( $\alpha$ CCs) from propargylic alcohols and CO<sub>2</sub> was reported in several manuscripts.<sup>19-23</sup> These  $\alpha$ CCs differed from conventional five-membered cyclic carbonates by the presence of an exomethylene moiety, and therefore combine two very useful functional groups: an activated cyclic carbonate and a vinyl group. The activated cyclic carbonate ring was shown to be easily opened by nucleophiles,<sup>17</sup> and this reactivity was recently exploited in polymer chemistry for the facile synthesis of functional regioregular poly(carbonate)s and poly(urethane)s by polyaddition of *bis*( $\alpha$ -alkylidene cyclic carbonate)s with diols and secondary/primary diamines, respectively.<sup>17</sup> The vinyl group, on the other hand, is prone to radical attack and can therefore be involved in radical (co)polymerisations. Amongst all  $\alpha$ CCs that were accessible, 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (DMMDO, Scheme 1) was highly attractive as it can be easily produced by organocatalysed coupling of CO<sub>2</sub> to 2-methyl-3-butyn-2-ol.<sup>22</sup> Nevertheless, the large steric hindrance induced by the two methyl groups at the 4-position rendered its homopolymerisation impossible at 60 °C.<sup>24,25</sup> The homopolymerisation was only possible above 120°C, however with the formation of oligomers ( $M_n = 2,100 \text{ g}\cdot\text{mol}^{-1}$ ) consisting of an alternating structure of cyclic carbonate and ketone units. These two structures originated from the occurrence of two different

radical polymerisation pathways: a radical ring-opening (rROP) polymerisation followed by decarboxylation that provided the polyketones (route a) and a vinyl-type polymerisation that resulted in polymers bearing pendant cyclic carbonates (route b) (Scheme 1).<sup>25</sup> The free radical copolymerisation of DMMDO with vinyl acetate (VAc) was reported to be possible at lower temperature (70 °C) *via* the vinyl-type polymerisation.<sup>24</sup> The absence of rROP was assumed to be the result of the lower copolymerisation temperature.



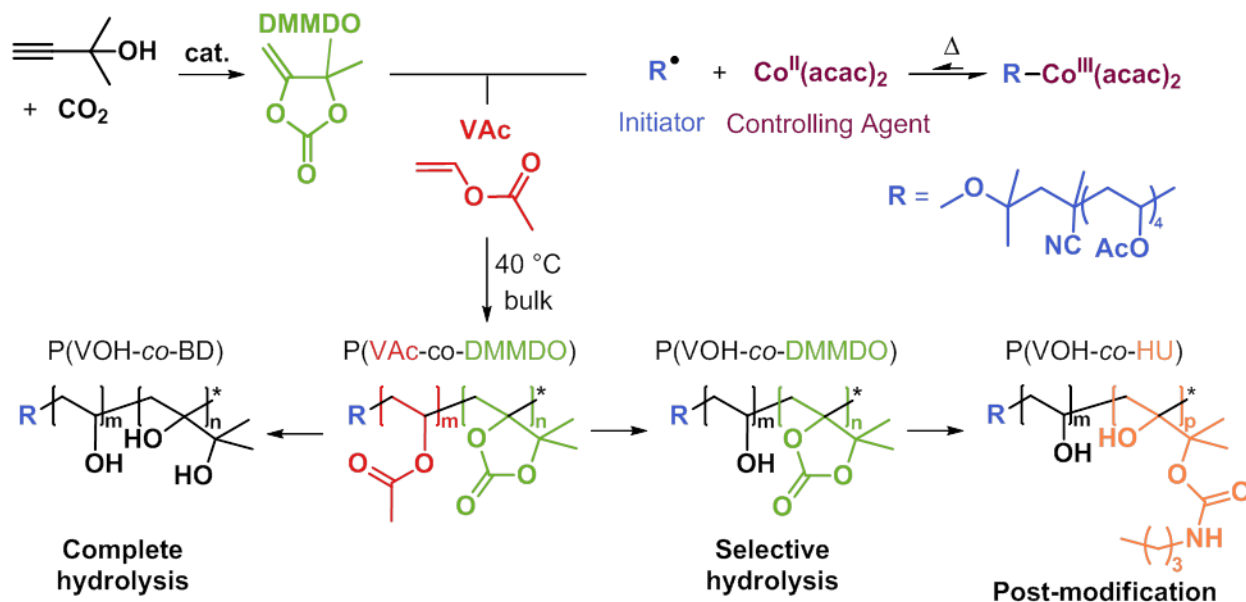
**Scheme 1.** Radical polymerisation of DMMDO and the reported occurrence of two polymerisation mechanisms: a) radical ring-opening polymerisation (rROP) and b) vinyl-type polymerisation (VT).

Polymers bearing pendant cyclic carbonate groups, prepared by radical (co)polymerisation of  $\alpha$ CCs, are attractive because they do not present any hydrolysable group between the polymer backbone and the CC ring, which is highly desirable for selective post-polymerisation modifications. The development of a controlled radical polymerisation technique for  $\alpha$ CCs that would disfavour rROP is thus needed for the precise synthesis of novel functional polymers. Only

a few studies reported on the controlled radical polymerisation of vinyl monomers bearing cyclic carbonates.<sup>26,27</sup> However, these works considered acrylate-type monomers that bear an ester function between the polymer backbone and the CC ring. Selective post-modifications of the CC rings were therefore challenging on those polymers because side reactions (such as hydrolysis or amidification) were expected to occur on the ester groups, prohibiting the production of the desired polymer.

In this work, we considered the copolymerisation of DMMDO with vinyl acetate (VAc) in order to provide novel well-defined poly(vinyl alcohol)-type (PVOH-type) copolymers by selective or complete hydrolysis of the P(VAc-*co*-DMMDO) precursor (Scheme 2). Indeed, PVOH is one of the most important industrial water-soluble synthetic polymers and the key ingredient in formulations of various products in food packaging, construction, electronics, coatings, printing, textile, cosmetics, and paper.<sup>28-30</sup> PVOH is commonly produced by methanolysis of poly(vinyl acetate) (PVAc) and the worldwide production capacity was estimated at 650 kT in 2015.<sup>28</sup> The precise localisation of CC groups along its polymer chain would bring new possibilities for further simple functionalisation and open new applications for this important polymer. This paper therefore describes the first controlled radical copolymerisation of this CO<sub>2</sub>-sourced monomer with VAc under experimental conditions that disfavour rROP. The reactivity ratios were determined in order to evaluate the distribution of the comonomers in the polymer, and the structure of the copolymer was thoroughly investigated. The conditions for the complete hydrolysis of the copolymer were then established to give a PVOH of high water solubility. The chemo-selective hydrolysis of the VAc units to provide PVOH bearing intact cyclic carbonate pendants was also investigated as well as its further post-polymerisation modification *via* the ring opening of the carbonate ring with butylamine. In contrast to classical PVOH-functionalisation

methods relying on the transformation of the pendant hydroxyl groups,<sup>31</sup> our post-modification strategy affords the advantage of preserving one hydroxyl group per repeat unit (Scheme 2).



**Scheme 2.** Cobalt-mediated radical polymerisation of VAc and DMMDO and subsequent hydrolysis and post-modification to yield functional PVOH.

## Experimental Section

**Materials:** Vinyl acetate (VAc, >99%, Aldrich) was dried over  $\text{CaH}_2$ , degassed by several freeze-pump-thaw cycles, distilled and stored at  $-20^\circ\text{C}$ . Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) was degassed and dried over  $4 \text{ \AA}$  molecular sieves. A previous literature procedure<sup>19</sup> for the synthesis of 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (DMMDO) was slightly modified: After the removal of triethylamine, the remaining zinc was removed by a silica oxide filter column and the product was purified by sublimation. Prior to use, the solid was degassed using 3 cycles of freeze-pump-thawing. Alkyl cobalt(III) adduct ( $[\text{Co}(\text{acac})_2(-\text{CH}(\text{OCOCH}_3)\text{CH}_2)_{<4}-\text{R}_0]$  with  $\text{R}_0$  being the primary radical generated by V-70; from now on  $\text{R-Co}(\text{acac})_2$ ) was prepared according to a

previous literature report and stored at  $-20\text{ }^{\circ}\text{C}$  in  $\text{CH}_2\text{Cl}_2$ .<sup>32</sup> N-butylamine (99.5% , Aldrich) and *N,N*-dimethylformamide (DMF, >99%, VWR) were dried over molecular sieves prior to use. 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO, 98%, Aldrich), triethylamine ( $\text{NEt}_3$ ,  $\geq 99\%$ , Aldrich), zinc iodide ( $\geq 98\%$ , Sigma), carbon dioxide ( $\text{CO}_2$ ,  $\geq 99.7\%$ , AirLiquide), sodium hydroxide ( $\text{NaOH}$ ,  $\geq 97\%$ , Acros), fuming hydrochloric acid ( $\text{HCl}$ , 37% solution, Acros), 1-propanethiol (99%, Aldrich), 1 kDa pre-treated regenerated cellulose tubing (Spectrum Laboratories, Inc.), silica gel for column chromatography (60 Å, ROCC S.A.), tetrahydrofuran (THF,  $\geq 99.9\%$ , VWR), methanol ( $\text{MeOH}$ ,  $\geq 99.8\%$ , VWR), n-pentane (>99.6%, VWR), diethyl ether (VWR,  $\text{Et}_2\text{O}$ ), dimethylsulfoxide (DMSO,  $\geq 99.9\%$ , VWR), deuterated dimethylsulfoxide ( $\text{DMSO-}d_6$ ,  $\geq 99.8\%$ , Euriso-top), deuterium oxide ( $\text{D}_2\text{O}$ ,  $\geq 99.9\%$  Euriso-top) and chloroform-*d* ( $\text{CDCl}_3$ , >99%, Euriso-top) were used as received. All polymerisations were performed under an inert atmosphere using Schlenk techniques.

**Copolymerisation of DMMDO with VAc.** A typical bulk VAc copolymerisation aiming at a  $f_{\text{DMMDO}} = 0.10$  (Entry 4, Table 1) was carried out at  $40\text{ }^{\circ}\text{C}$  using a molar ratio of  $[\text{VAc}]_0/[\text{DMMDO}]_0/[\text{R-Co}(\text{acac})_2]_0 = 360/40/1$ . A solution of  $\text{R-Co}(\text{acac})_2$  (0.6 mL; 0.1136 M stock solution in  $\text{CH}_2\text{Cl}_2$ , 0.06816 mmol) was introduced under argon into a purged 30 mL Schlenk tube and evaporated to dryness under reduced pressure at room temperature. VAc (2.3 mL, 25.0 mmol) was added under argon to give solution **A**. In a second 30 mL Schlenk tube, 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (DMMDO; 0.2911 g, 2.27 mmol) was added and heated to  $40\text{ }^{\circ}\text{C}$  and stirred at 500 rpm. 1.9 mL of solution **A** were transferred to this second Schlenk tube using a syringe under argon atmosphere and an  $^1\text{H-NMR}$  spectroscopy aliquot was immediately taken to determine the monomer feed ratio. The copolymerisation occurred at  $40\text{ }^{\circ}\text{C}$  under stirring. At regular intervals, aliquots of the reaction mixture were taken for NMR and SEC

analyses to determine conversions and the molecular parameters of the polymer, respectively. The  $M_n$  of these non-precipitated reaction mixtures was determined by integrating the copolymer peak while excluding the small peak originating from deactivated R-Co(acac)<sub>2</sub>. When the polymers were precipitated, this small peak was not present. After 25 hours, the reaction mixture was quenched using a degassed solution of TEMPO (150 mg, 1 mmol) in 2 mL of THF and was passed over a micro silica column to remove the cleaved cobalt. The polymer was then precipitated three times in n-pentane (~200 mL) from THF and dried overnight under vacuum at 50 °C.

For the polymer to be analysed by MALDI-TOF, a molar ratio of [VAc]<sub>0</sub>/[DMMDO]<sub>0</sub>/[R-Co(acac)<sub>2</sub>]<sub>0</sub> = 90/10/1 was used and a solution of R-Co(acac)<sub>2</sub> (1.33 mL; 0.1710 M stock solution in CH<sub>2</sub>Cl<sub>2</sub>, 0.2272 mmol) was introduced under argon into a purged 30 mL Schlenk tube and evaporated to dryness under reduced pressure at room temperature. VAc (1.9 mL, 20.6 mmol) was added under argon and the solution was added to a second 30 mL Schlenk tube, in which 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (DMMDO; 0.2911 g, 2.27 mmol) had been added. The reaction mixture was heated to 40 °C at 500 rpm stirring. A <sup>1</sup>H-NMR spectroscopy aliquot was immediately taken to determine the monomer feed ratio. The copolymerisation occurred at 40 °C under stirring and after 6 hours of polymerisation at 42% overall conversion, ~1 mL of the reaction mixture was transferred to a purged Schlenk containing propanethiol (1 mL, 11 mmol) and allowed to react for 1 hour, dried under vacuum, then dissolved in THF and passed over 0.45 μm filter to remove the thiol-cobalt complex and finally dried under vacuum at 50 °C. The remaining reaction solution was purified as previously described and analysed using NMR spectroscopy, FT-IR and SEC.

100 mg of the copolymer (Entry 12, Table S1) to be analysed by the ICP-OE spectrometer were added to 2 mL of HNO<sub>3</sub> and allowed to react for 2 hours at 65 °C. After dilution with 10 mL of



distilled water, the solution was filtered, filled into a 25 mL volumetric flask and made up to 25 mL.

**Determination of reactivity ratios:** Reactivity ratios were determined by using both V-70 and R-Co(acac)<sub>2</sub> as the initiator and molar ratios of monomer to initiator of 400:0.5 and 400:1 were used respectively. Using CMRP, the same protocol as above was used, while for free radical polymerisations using V-70, reaction feeds ranged from 10 to 80 mol% of DMMDO. A typical reaction with a molar ratio of 10 : 90 of DMMDO:VAc was performed as follows: In a 15 mL Schlenk flask, V-70 (8.8 mg, 0.0284 mmol) and DMMDO (0.2911 g, 2.27 mmol) were weighed out and degassed three times using freeze-pump-thawing. The Schlenk flask was heated to 40 °C at 500 rpm stirring and VAc (2.3 mL, 2.5 mmol) was added. A <sup>1</sup>H-NMR sample was immediately taken to determine the feed of the reaction. In order to stop the reactions at conversions below 15%, the reaction was monitored by taking aliquots and precipitating these in a small amount of n-pentane (20 mL). Once a precipitate was observed, a <sup>1</sup>H-NMR sample was taken of the reaction mixture to determine the conversion and the reaction was quenched using TEMPO/THF (150 mg, 1 mmol; in 2 mL). The polymer was precipitated three times into n-pentane (200 mL) from THF for feeds below 50 mol% DMMDO and 5 times above 50 mol%. The polymer was then dried in vacuum overnight at 50 °C. SEC and <sup>1</sup>H-NMR spectroscopy analysis were performed to determine the molecular parameters and the composition of the polymer. The reaction time, feed of the polymerisation medium, conversion and composition of the copolymer were used to create different plots according to Kelen-Tüdös and the Mayo-Lewis equation (Equations 1-2).<sup>33-35</sup> The Kelen-Tüdös linearisation can be obtained from the Mayo-Lewis equation (Equation 1). Using the mole ratios of the monomers in the feed (*f*) and in the copolymer (*F*) along with

parameter  $\alpha$  ( $f^2/F$ ) two mathematical functions  $\zeta$  and  $\eta$  (Equation 2) were created. A linear plot of  $\eta$  as a function of  $\zeta$  leads to  $r_1$  and  $(-r_2/\alpha)$  via the intercepts at  $\zeta = 1$  and  $\zeta = 0$ , respectively.

$$F_1 = (r_1 f_1^2 + f_1 f_2) / (r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2) \quad (1)$$

$$\eta = (r_1 + (r_2/\alpha)) \zeta - (r_2/\alpha) \quad (2)$$

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

$$\eta = (f(F-1)) / (F(\alpha + (f^2/F)))$$

$$\zeta = (f^2/F) / (\alpha + (f^2/F))$$

$$\alpha = ((f^2/F)_{\max} \times (f^2/F)_{\min})^{0.5}$$

Using the above determined reactivity ratios, the Skeist model<sup>36</sup> was applied, which allows to predict the instantaneous and cumulative copolymer composition as well as the instantaneous feed (Equation 3).

$$Conversion = 1 - (M/M_0) = 1 - (f_1/f_1^0)^\alpha (f_2/f_2^0)^\beta [(f_1^0 - \delta)/(f_1 - \delta)]^\gamma \quad (3)$$

where  $M_0$  and  $M$  are the initial and instantaneous monomer concentrations and  $f^0$  and  $f$  correspond to the initial and instantaneous molar fractions of the monomers in the feed, respectively.  $\alpha$ ,  $\beta$ ,  $\delta$  and  $\gamma$  are defined as  $\alpha = r_2/(1-r_2)$ ,  $\beta = r_1/(1-r_1)$ ,  $\gamma = (1-r_1 r_2)/(1-r_1)(1-r_2)$ , and  $\delta = (1-r_2)/(2-r_1-r_2)$ . The cumulative copolymer composition was calculated using:  $F_{1 \text{ cumul}} = [f_1^0 - f_1 (1 - \text{conversion})] / \text{conversion}$

**Hydrolysis and methanolysis of P(VAc-co-DMMDO).** Both acidic and basic hydrolysis were performed on a copolymer containing 21 mol% DMMDO ( $M_n = 18,400 \text{ g}\cdot\text{mol}^{-1}$ ,  $M_w/M_n = 1.29$ ; Table S1, Entry 10).

*Acidic hydrolysis.* 500 mg of the copolymer were dissolved in 5 mL of THF and added to a 25 mL round bottom flask. 5 mL of deionised water and 0.5 mL of concentrated, fuming HCl (37% solution, 6.038 mmol) were added and the solution was refluxed at 90 °C for 48 hours at 500 rpm. An orange-yellow solution was obtained. The reaction mixture was neutralised using a 1M NaOH solution and transferred to a 1 kDa regenerated cellulose dialysis tubing, which was dialysed in a water/MeOH mixture starting with 30 vol% of water, then 20 vol%, 5% and pure methanol. The solution was lyophilised to obtain 192.1 mg of a bright yellow solid. FT-IR:  $\nu_{\max}$ : 3330  $\text{cm}^{-1}$  (b, OH stretch); 2900  $\text{cm}^{-1}$  (b, C-H stretch); 1780  $\text{cm}^{-1}$  (s, -O-(C=O)-O- stretch).  $^{13}\text{C}$ -NMR (400 MHz, DMSO- $d_6$ ): 170 ppm (-O-(C=O)-O-); 90 ppm ( $\text{CH}_2$ -C-C-( $\text{CH}_3$ ) $_2$ -); 65 ppm (-C-H-OH); 47 ppm (-CH $_2$ -CH-OH); 40 ppm (-CH $_2$ -C-O-); 22 ppm (-C-CH $_3$ ). The  $^1\text{H}$ -NMR peaks are assigned in Figure 9.

*Methanolysis.* 3.7 g NaOH (0.093 mol) were dissolved in 150 mL MeOH in a 250 mL round-bottom flask, to which 500 mg of the copolymer dissolved in 5 mL of THF were added. The mixture was refluxed at 65 °C for 24 hours at 500 rpm. The resulting solution was neutralised using a 1M HCl solution, stripped of its solvent until around 15 mL remained and dialysed using 1kDa regenerated cellulose tubing in a water/MeOH mixture starting with 30 vol% of water, then 20 vol%, 5% and pure methanol. The solution was lyophilised to obtain 123.6 mg of a brick-red powder. FT-IR: 3330  $\text{cm}^{-1}$  (b, OH stretch); 2900  $\text{cm}^{-1}$  (b, C-H stretch).  $^{13}\text{C}$ -NMR (400 MHz, DMSO- $d_6$ ): 65 ppm (-C-H-OH); 45 ppm (-CH $_2$ -CH-OH and -CH $_2$ -C-O-); 22 ppm (-C-CH $_3$ ). The  $^1\text{H}$ -NMR peaks are assigned in Figure 9.

To compare the influence of the comonomer on the polymer characteristics, a copolymer and a PVAc homopolymer of equivalent DP were synthesised (Table S3, Entry 1 and 2). The copolymer was hydrolysed as outlined above, while 1 g of the PVAc homopolymer was methanolysed using 0.25 g KOH in 60 mL MeOH at room temperature for 24 hours, as

previously described.<sup>37</sup> After filtration and dialysis in water using 1kDa tubing and subsequent lyophilisation, 446 mg of a white solid were obtained. The methanolysed copolymer (P(VOH-co-BD)) and PVOH were dissolved in 0.5 mL water at different concentrations (1, 10, 25, 50, 150, 375 g/L) and the temperature increased from 20 °C to 80 °C, noting the temperature at which the polymer solubilised (Table S4).

**Post-polymerisation modification of selectively hydrolysed copolymer:** A P(DMMDO-co-VAc) copolymer (Table S1, entry 12) subjected to acidic/selective hydrolysis was post-modified using butylamine. 100 mg of P(DMMDO-co-VOH) and 2 mg of TBD (0.01 mmol) were dissolved in 0.5 mL of dry butylamine (0.37 g, 5.059 mmol) and 0.5 mL dry DMF and heated to 80 °C for 24 hours in a Schlenk flask. The reaction mixture was precipitated into 100 mL cold diethyl ether, dialysed in MeOH using a 1 kDa cellulose tubing and then lyophilised to remove residual solvent. The obtained 85 mg of modified copolymer were analysed by NMR spectroscopy and FT-IR.

**Characterisations.** <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy were performed on 250, 400 MHz Bruker instruments at room temperature using chloroform-*d* (CDCl<sub>3</sub>), deuterated water (D<sub>2</sub>O) or dimethyl sulfoxide-*d*<sub>6</sub> (DMSO-*d*<sub>6</sub>). The chemical shifts ( $\delta$ ) are reported in parts per million (ppm). For all the kinetic experiments, the consumption of VAc during the reaction was determined by comparing the integrals of the <sup>1</sup>H-NMR spectroscopy peak centred at 4.89 ppm corresponding to one proton of the  $-\underline{CH}_2-$  of the monomer VAc and the  $-\underline{CH}-OAc$  in the copolymer ( $\int_{4.62}^{5.40} Pol(CH) + Mon(CH)$ ) with the peak centred at 4.58 ppm corresponding to the  $-\underline{CH}-OAc$  of only the monomer VAc ( $\int_{4.44}^{4.62} Mon(CH)$ , Equation 4). Since one of the symmetric

vinyl  $-\underline{CH}$  peaks of DMMDO overlaps with the peak centred at 4.89 ppm, the integral of the other  $-\underline{CH}$  peak of DMMDO at 4.32 ppm ( $\int_{4.20}^{4.44} DMMDO(CH)$ ) is subtracted (Equation 4). For the conversion of DMMDO, the monomer  $-\underline{CH}_3$  peak at 1.50 - 1.70 ppm ( $\int_{1.50}^{1.70} Mon(CH_3)$ ) was integrated with respect to a broad doublet at 1.50-1.34 ppm corresponding to the two  $-\underline{CH}_3$  environments in the polymer ( $\int_{1.34}^{1.50} Pol(CH_3)$ ); Equation 5).

$$\% VAc\ conversion = \left( 1 - \frac{\int_{4.44}^{4.62} Mon(CH)}{\int_{4.62}^{5.40} Pol(CH) + Mon(CH) - \int_{4.20}^{4.44} DMMDO(CH)} \right) \times 100 \quad (4)$$

$$\% DMMDO\ conversion = \frac{\int_{1.34}^{1.50} Pol(CH_3)}{\int_{1.50}^{1.70} Mon(CH_3)} \times 100 \quad (5)$$

where  $\int_m^n CH_x$  is the integral of the  $CH_x$  environment from  $m$  ppm to  $n$  ppm.

The theoretical molecular weight ( $M_{n\ theo}$ ) was calculated by adding the molecular weight of the initiator fragment ( $M_{w\ init} = 485.57\ g.mol^{-1}$ ) and the TEMPO chain-end ( $M_{w\ TEMPO} = 156.25\ g.mol^{-1}$ ) to the molecular weight of the copolymer chain ( $M_{n\ chain}$ ) which was calculated using the conversion of VAc and DMMDO according to the equation below:

$$M_{n\ chain} = M_{w\ VAc} \times Conv_{VAc} \times f_{VAc}^0 + M_{w\ DMMDO} \times Conv_{DMMDO} \times f_{DMMDO}^0 \quad (6)$$

Where  $M_{w\ Mon}$  is the molecular weight of the monomer in  $g.mol^{-1}$ ,  $Conv_{Mon}$  is the conversion of the monomer and  $f_{Mon}^0$  is the initial feed of the monomer in the reaction mixture.

$$M_{n\ theo} = M_{w\ init} + M_{w\ TEMPO} + M_{n\ chain} \quad (7)$$

The copolymer composition of P(VAc-co-DMMDO) was determined by  $^1H$ -NMR spectroscopy of the purified polymers in  $CDCl_3$  (Figure S2). The degree of polymerisation of VAc ( $DP_{VAc}$ ) was determined by  $^1H$ -NMR spectroscopy by comparing the integrals of the methoxy groups (O-

$CH_3$ ) ( $\int_{3.05}^{3.25} OCH_3$ ) at the  $\alpha$ -chain end at 3.15 ppm with the integral of  $-CH-$  of the VAc repeating unit ( $-CH_2-CHOAc$ ) ( $\int_{4.5}^{5.6} CH$ ) at 4.8 ppm. The equation to determine  $DP_{VAc}$  is:

$$DP \text{ of VAc} = \int_{4.5}^{5.6} CH / \left( \frac{\int_{3.05}^{3.25} OCH_3}{3} \right) \quad (8)$$

The DP of DMMDO ( $DP_{DMMDO}$ ) was determined by comparing the integrals of the methoxy groups ( $-OCH_3$ ) ( $\int_{3.05}^{3.25} OCH_3$ ) at the  $\alpha$ -chain end at 3.15 ppm with the integral of all protons from 2.6 - 1.2 ppm ( $\int_{1.2}^{2.6} H$ ; corresponding to 5H of VAc unit ( $-\underline{CH_2}-CHOC(=O)\underline{CH_3}$ ) + 8H of DMMDO unit ( $-\underline{CH_2}-C-C(\underline{CH_3})_2-O-C(=O)-O-$ ) + 11H of the initiating fragment ( $CH_3O-C(\underline{CH_3})_2-\underline{CH_2}-C(\underline{CH_3})(CN)-$ ). The equation to determine  $DP_{DMMDO}$  is:

$$DP \text{ of DMMDO} = \left( \frac{\int_{1.2}^{2.6} H - 5 \times \int_{4.5}^{5.6} CH - 11 \times \left( \frac{\int_{3.05}^{3.25} OCH_3}{3} \right)}{8} \right) / \left( \frac{\int_{3.05}^{3.25} OCH_3}{3} \right) \quad (9)$$

The copolymer composition of P(VOH-*co*-DMMDO) was determined by  $^1H$ -NMR spectroscopy of the purified polymers in DMSO- $d_6$  (Figure S2). The DP of VOH ( $DP_{VOH}$ ) was identical to  $DP_{VAc}$  of the starting P(VAc-*co*-DMMDO). The DP of DMMDO ( $DP_{DMMDO}$ ) was determined by comparing the integrals of the VOH unit ( $-CH_2-\underline{CH}(OH)-$ ) at 3.8 ppm ( $\int_{3.5}^{4.1} CH(OH)$ ) with the integral of the DMMDO unit (2H;  $-\underline{CH_2}-C-C(\underline{CH_3})_2-O-C(=O)-O-$ ) ( $\int_{1.80}^{2.28} CH_2$ ) by the following equation:

$$DP \text{ of DMMDO} = (DP_{VOH} \times \left( \frac{\int_{1.80}^{2.28} CH_2}{2} \right)) / \int_{3.5}^{4.1} CH(OH) \quad (10)$$

The copolymer composition of P(VOH-*co*-DMMDO-*co*-HU) was determined by  $^1H$ -NMR spectroscopy of the purified polymers in MeOD- $d_4$  (Figure S5). The DP of VOH ( $DP_{VOH}$ ) was

identical to  $DP_{VAc}$  of the starting P(VAc-co-DMMDO). The DP of HU units ( $DP_{HU}$ ) was determined by comparing the integrals of the VOH unit ( $-CH_2-\underline{CH}(OH)-$ ) at 4 ppm ( $\int_{3.68}^{4.48} CH(OH)$ ) with the integral of HU unit ( $\int_{3.02}^{3.24} NHCH_2$ ) which includes the three protons of the methoxy groups of the  $\alpha$ -chain end (3H,  $-OCH_3$ ) and the two protons next to the amine function (2H;  $-CH_2-C(OH)-C(CH_3)_2-O-C(=O)-NH-\underline{CH_2}-(CH_2)_2-CH_3$ ) by the following equation:

$$DP \text{ of HU} = (DP_{VOH} \times \frac{\int_{3.02}^{3.24} NHCH_2 - 3H(OCH_3)}{2}) / \int_{3.68}^{4.48} CH(OH) \quad (11)$$

The DP of DMMDO ( $DP_{DMMDO}$ ) in P(VOH-co-DMMDO-co-HU) was determined by comparing the integrals of the VOH unit ( $-CH_2-\underline{CH}(OH)-$ ) at 4 ppm with the integral of HU unit ( $\int_{3.02}^{3.24} NHCH_2$ ) which includes the three protons of the methoxy groups of the  $\alpha$ -chain end (3H,  $-OCH_3$ ) and the two protons next to the amine function (2H;  $-CH_2-C(OH)-C(CH_3)_2-O-C(=O)-NH-\underline{CH_2}-(CH_2)_2-CH_3$ ), and the integral of all protons between 0.9 and 2.4 ppm ( $\int_{0.9}^{2.4} H$ ; corresponding to 2H of VOH unit ( $-\underline{CH_2}-CH(OH)$ ) + 8H of DMMDO unit ( $-\underline{CH_2}-C-C(CH_3)_2-O-C(=O)-O-$ ) + 15H of HU unit ( $-\underline{CH_2}-C(OH)-C(CH_3)_2-O-C(=O)-NH-CH_2-\underline{(CH_2)_2-CH_3}$ ) + 11H of the initiating fragment ( $CH_3O-C(CH_3)_2-\underline{CH_2}-C(CH_3)(CN)-$ ) by the following equation:

$$DP \text{ of DMMDO} = (DP_{VOH} \times \frac{(\int_{0.9}^{2.4} H - (\int_{3.68}^{4.48} CH(OH) \times 2 - (\frac{\int_{3.02}^{3.24} NHCH_2 - 3H(OCH_3)}{2} \times 15))}{8}) / \int_{3.68}^{4.48} CH(OH) \quad (12)$$

Fourier-transform infrared analysis (FT-IR) was performed on a ThermoFisher Scientific Nicolet IS5 with module ATR ID5 using a diamond crystal ( $650 \text{ cm}^{-1} - 4000 \text{ cm}^{-1}$ ).

Differential scanning calorimetry (DSC) was performed on a DSC Q100 instrument from TA Instruments by placing around 5 mg of sample in an aluminium pan. The sample was cooled to 0

°C, then heated to 140 °C, cooled to -90 °C and heated to 130 °C at a heating/cooling rate of 10 °C/min. The last heating cycle was used for the determination of the  $T_g$ .

Thermogravimetric analysis (TGA) was performed on a TGA Q500 instrument from TA Instruments. Around 5 mg of sample were heated to 100 °C, held there for 10 minutes to remove any remaining solvent and then heated to 600 °C.

Size-exclusion chromatography (SEC) was carried out in THF at 45 °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 polystyrene standards and a refractive index detector.

Matrix Assisted Laser Desorption/Ionisation Time-of-Flight (MALDI-ToF) mass spectra were recorded using a Waters QToF Premier mass spectrometer equipped with a Nd:YAG laser using the 3<sup>rd</sup> harmonic with a wavelength of 355 nm. In the context of this study, a maximum output of ~65 J was delivered to the sample in 2.2 ns pulses at 50 Hz repeating rate. Time-of-flight mass analyses were performed in reflection mode. The matrix, trans-2-[3-(4-tert-butyl-phenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), was prepared as a 40 mg/mL solution in chloroform. The matrix solution (1 µL) was applied to a stainless steel MALDI target and air-dried. Polymer samples were dissolved in THF to obtain 1 mg/mL solutions and 20 µL of NaI solution (2 mg/mL in acetonitrile) are added as source of cationisation agent. Then, 1 µL aliquots of these solutions were applied onto the target area (already bearing the matrix crystals) and then air-dried.<sup>38</sup>

Inductively coupled plasma optical emission spectrometry (ICP-OES) was performed on a Varian 720-ES. A calibration window of 1-200 mg/L was established using dilutions of a Certipur standard solution (1000 mg/L in Co, Merck).



## Results and Discussion

The choice of the polymerisation technique for the copolymerisation of DMMDO with VAc was of particular importance if rROP of DMMDO is to be avoided (see discussion in the introduction). As rROP is favoured at high temperature, mild experimental conditions had to be implemented for this copolymerisation that involves two less-activated monomers (LAMs).<sup>39</sup> This prompted us to use the cobalt-mediated radical polymerisation (CMRP) technique mediated by Co(acac)<sub>2</sub> as it is highly active for the VAc polymerisation and its copolymerisation with various families of monomers (acrylonitrile, acrylates, ethylene, *N*-vinyl amides, vinylidene fluoride, etc.) is feasible.<sup>40-49</sup> Moreover, CMRP is active at low temperature, i.e. 0-40 °C depending on the comonomers, which is of prime importance for avoiding rROP and thus yielding copolymers with intact CC-rings (Scheme 2).

**Controlled statistical copolymerisation.** To the best of our knowledge, the copolymerisation of DMMDO/VAc has not been reported before using any controlled radical polymerisation technique. The DMMDO/VAc copolymerisation was investigated by using a preformed alkylcobalt(III) acetylacetonate (R-Co(acac)<sub>2</sub>) complex, where the alkyl chain acts as the radical initiator and Co(acac)<sub>2</sub> as the controlling agent (Scheme 2).<sup>32</sup> First, a degree of polymerisation of 400 was targeted for various comonomer feeds ranging from 5 to 40 mol% DMMDO ( $f_{\text{DMMDO}} = 0.05 - 0.40$ ) at 40 °C in the bulk. It was observed that the molar masses of the polymers increased linearly with the monomer conversion, while retaining low dispersities throughout the polymerisation (Table 1, Figure 1a). Figure 1c shows that the SEC traces of the crude product were completely shifted towards higher molecular weights with monomer conversion, with only a very small tailing at the low molar mass side for the last sample. The small peak at around 20 min in the SEC trace corresponds to some deactivated R-Co(acac)<sub>2</sub> that was removed once the

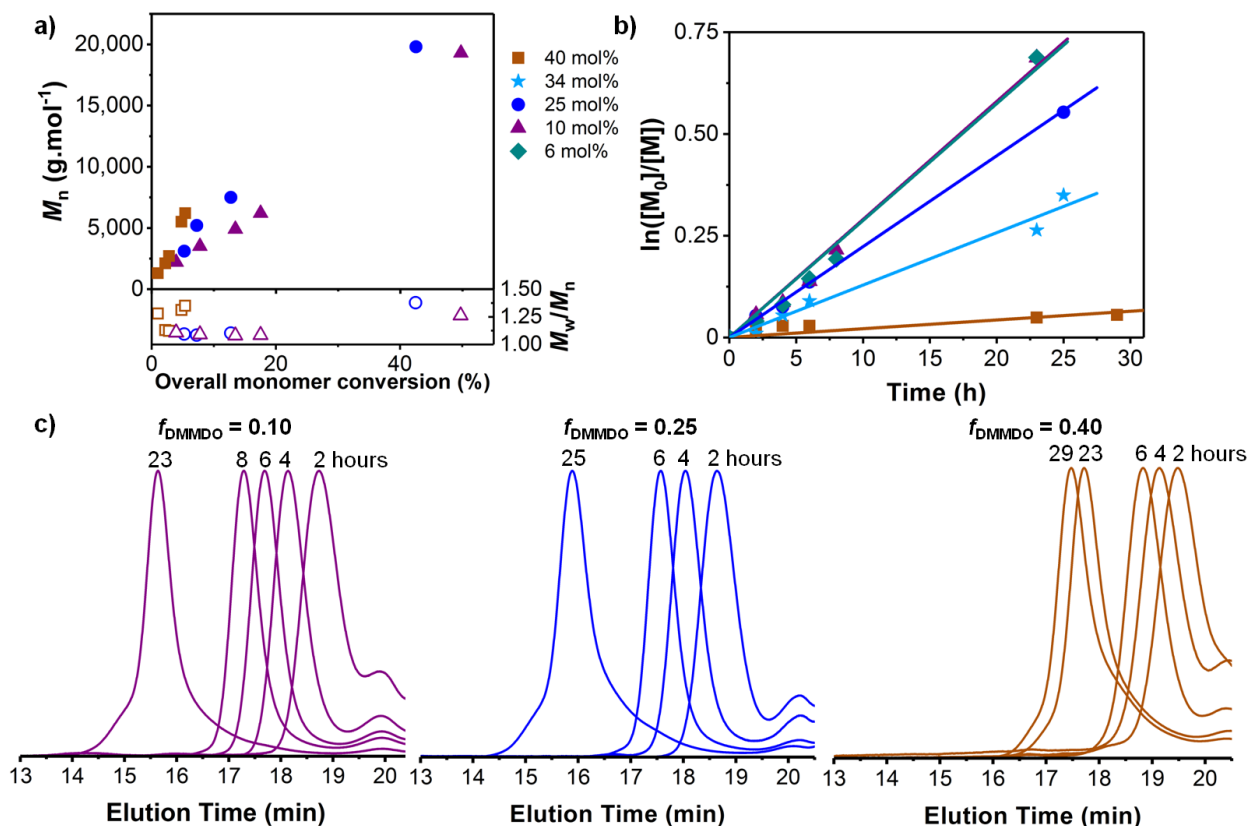
polymer was precipitated. The linear pseudo-first order kinetic plot highlights a decrease in the rate of polymerisation with an increasing feed in DMMDO (Figure 1b). For instance, under identical polymerisation conditions, a conversion of 83% was observed for the homopolymerisation of VAc after 23 hours of reaction compared to 50% or 30% when 6 or 34 mol% DMMDO were present, respectively (comparison of entries 1, 3 and 6, Table 1). Copolymerisation feeds above 40 mol% DMMDO were also investigated, but for  $f_{\text{DMMDO}} > 0.50$ , the monomer conversion was limited to a few percent (Entry 8, Table S1). The origin of this inhibition is not yet understood. The homopolymerisation of DMMDO was not observed using R-Co(acac)<sub>2</sub> (Entry 2, Table 1), which is in agreement with the absence of homopolymer under free-radical polymerisation conditions.<sup>24,25</sup> To accelerate the copolymerisation, 20 equivalents of water (compared to R-Co(acac)<sub>2</sub>) were added and indeed the total conversion increased from 5% to 17% when about 40 mol% DMMDO was used in the feed (Entries 7 and 8, Table 1). As previously reported,<sup>32,48,50</sup> water is assumed to slightly shift the active/dormant species equilibrium towards the active side by complexing the deactivating (Co(acac)<sub>2</sub>) species into Co(acac)<sub>2</sub>L and Co(acac)<sub>2</sub>L<sub>2</sub> (where L is water).

The molar mass of the copolymer can also be adjusted by tuning the monomers M/R-Co(acac)<sub>2</sub> molar ratio. For instance, for a feed content of about 15 mol% DMMDO and a M/R-Co(acac)<sub>2</sub> ratio of 100, a copolymer with molecular weight of 3,900 g.mol<sup>-1</sup> and a dispersity of 1.10 was obtained (Entry 9, Table 1). Experimental molar masses determined by <sup>1</sup>H-NMR based on the  $\alpha$ -chain-end ( $M_{\text{n NMR}}$ , see experimental section for details) were also affected in a similar way by the M/R-Co(acac)<sub>2</sub> molar ratio (comparison of Entries 4 and 9, Table 1). It is worth noting that the differences in molar mass values noted in some cases between theoretical molar masses ( $M_{\text{n th}}$ ) and  $M_{\text{n NMR}}$  notably originate from inaccuracy on both the determination of the monomer conversion and on the integration of the  $\alpha$ -chain-end .

**Table 1.** Copolymerisations of VAc and DMMDO using R-Co(acac)<sub>2</sub> at 40°C<sup>g</sup>

Entry	$f_{\text{VAc}}^0$	Time	Total	Composition	$M_{\text{n theo}}$	$M_{\text{n NMR}}$	$M_{\text{n SEC}}$	$M_{\text{w}}/M_{\text{n}}^{\text{d}}$
	$f_{\text{DMMDO}}^{\text{a}}$	(h)	conversion	( $F_{\text{VAc}}/$	(g.mol <sup>-1</sup> ) <sup>c</sup>	(g.mol <sup>-1</sup> ) <sup>b</sup>	(g.mol <sup>-1</sup> ) <sup>d</sup>	
			(%) <sup>a</sup>	$F_{\text{DMMDO}}^{\text{b}}$				
1	1/0	23	83	1/0	29,200	29,000	29,300	1.30
2	0/1	23	0	-	-	-	-	-
3	0.94/0.06	23	50	0.89/0.11	18,100	17,500	19,300	1.26
4	0.88/0.12	23	52	0.87/0.13	20,000	25,100	24,800	1.32
5	0.75/0.25	25	45	0.83/0.16	18,000	24,900	19,800	1.37
6	0.66/0.34	25	30	0.78/0.22	11,500	14,400	13,600	1.29
7	0.60/0.40	29	6	0.60/0.40	n.d.	9,300	6,200	1.35
8 <sup>e</sup>	0.57/0.43	29	26	0.67/0.33	10,800	17,800	15,200	1.33
9 <sup>f</sup>	0.85/0.15	6	42	0.86/0.16	4,400	4,300	3,900	1.10

Conditions: bulk, M/R-Co(acac)<sub>2</sub> = 400/1, magnetic stirring at 500 rpm. <sup>a</sup> Determined by <sup>1</sup>H-NMR spectroscopy in CDCl<sub>3</sub>. <sup>b</sup> Composition of the copolymer and molecular weight determined by <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub> based on the  $\alpha$ -chain end (see experimental section). <sup>c</sup>  $M_{\text{n theo}} = M_{\text{w init}} + (\text{Conv}_{\text{DMMDO}} \times M_{\text{w DMMDO}} + \text{Conv}_{\text{VAc}} \times M_{\text{w VAc}}) + M_{\text{w TEMPO}}$  (for more information see experimental section). <sup>d</sup> Determined by size exclusion chromatography (SEC) in THF using PS standard. <sup>e</sup> Addition of H<sub>2</sub>O, R-Co(acac)<sub>2</sub>/H<sub>2</sub>O = 1/20. <sup>f</sup> Conditions: bulk, M/R-Co = 100, magnetic stirring at 500 rpm. <sup>g</sup> Full kinetics are in Supporting Information (Table S1). n.d.: not determined.



**Figure 1.** CMRPs at 40 °C of DMMDO and VAc at  $f_{\text{DMMDO}}^0$  ranging from 6 to 40 mol%: a)  $M_n$  and dispersity vs. total monomer conversion plot, b) first-order kinetic logarithmic plot with linear fits and c) size exclusion traces of kinetics with initial DMMDO feeds of 10, 25 and 40 mol%.

We then turned our attention to the copolymer structure since previously reported free radical copolymerisations of DMMDO yielded two possible structures: a combination of polyketones and intact cyclic carbonates when rROP, followed by decarboxylation, occurred in conjunction with a vinyl-type mechanism, and a polymer bearing exclusively intact cyclic carbonates when propagation occurred by radical addition on the double bond in the absence of rROP (Scheme 1).<sup>24,25</sup>  $^{13}\text{C}$ -NMR spectroscopy strongly indicated that the polymers prepared in this study

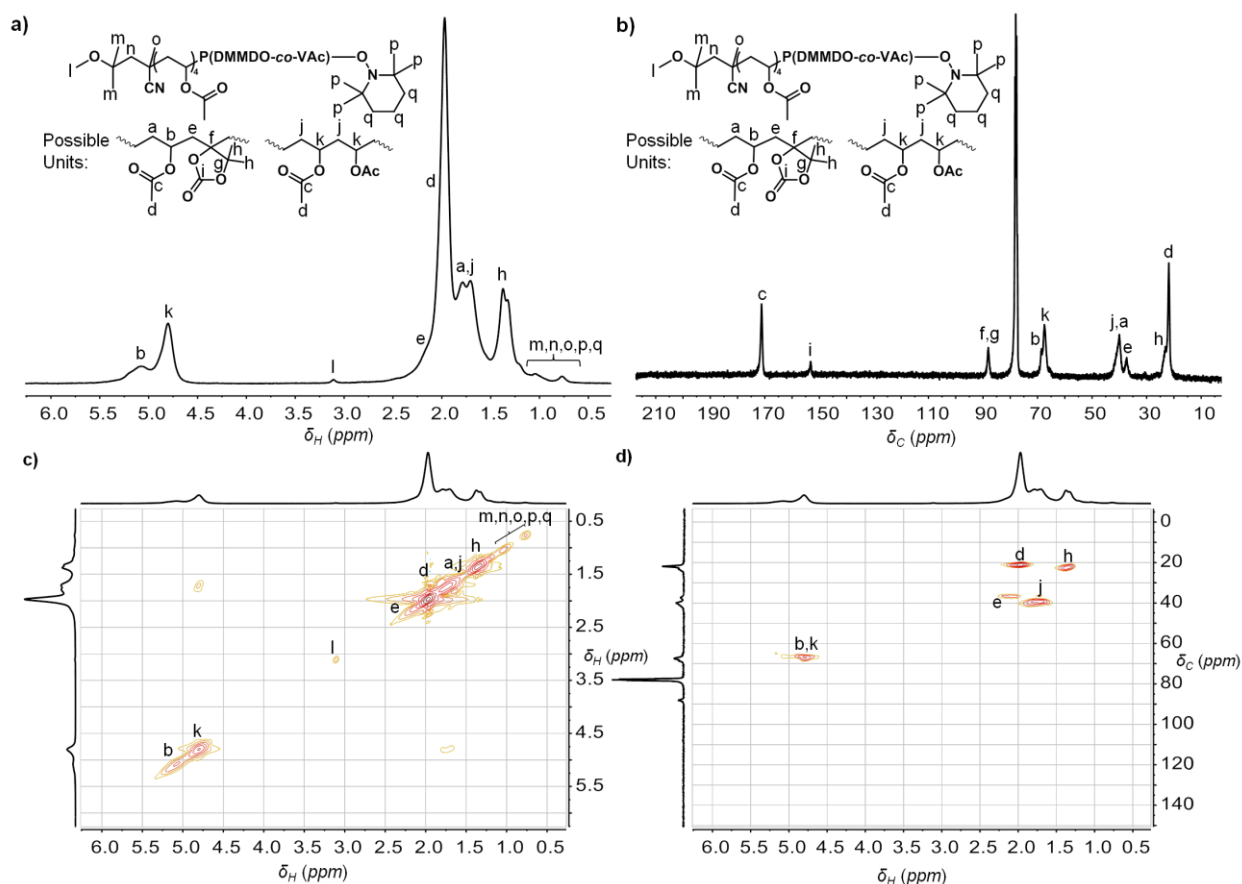
exclusively contain the intact carbonate ring with the characteristic carbonate peak at 152 ppm and the absence of a ketone signal at 210 ppm that may arise from rROP (Figure 2b). Additionally, by IR spectroscopy, two important bands were observed in the carbonyl region, one at 1730  $\text{cm}^{-1}$  that was assigned to the ester group of the vinyl acetate repeating units, and one at 1800  $\text{cm}^{-1}$  that was attributed to the carbonate stretching (Figure S1). The latter was unchanged in terms of wavenumber with respect to the monomer and these results reinforced the proposed structure of the copolymer.

Further evidence for the proposed structure was obtained by performing MALDI-ToF analysis on a low molar mass copolymer (Entry 9, Table 1). As presented in Figure 3a, the copolymer is characterised by one narrow distribution centred around  $m/z$  3650. The presence of signals separated by 128 mass units (u), characteristic of the DMMDO unit bearing the CC unit, and 86u, the mass of the VAc monomer unit, confirmed the incorporation of both monomers into the polymer backbone. As an illustration, theoretical models for copolymers with 36 ( $\text{VAc}_{33}:\text{DMMDO}_3$ ) and 37 ( $\text{VAc}_{33}:\text{DMMDO}_4$ ) monomer units are presented and match the experimental data (Figure 3b).

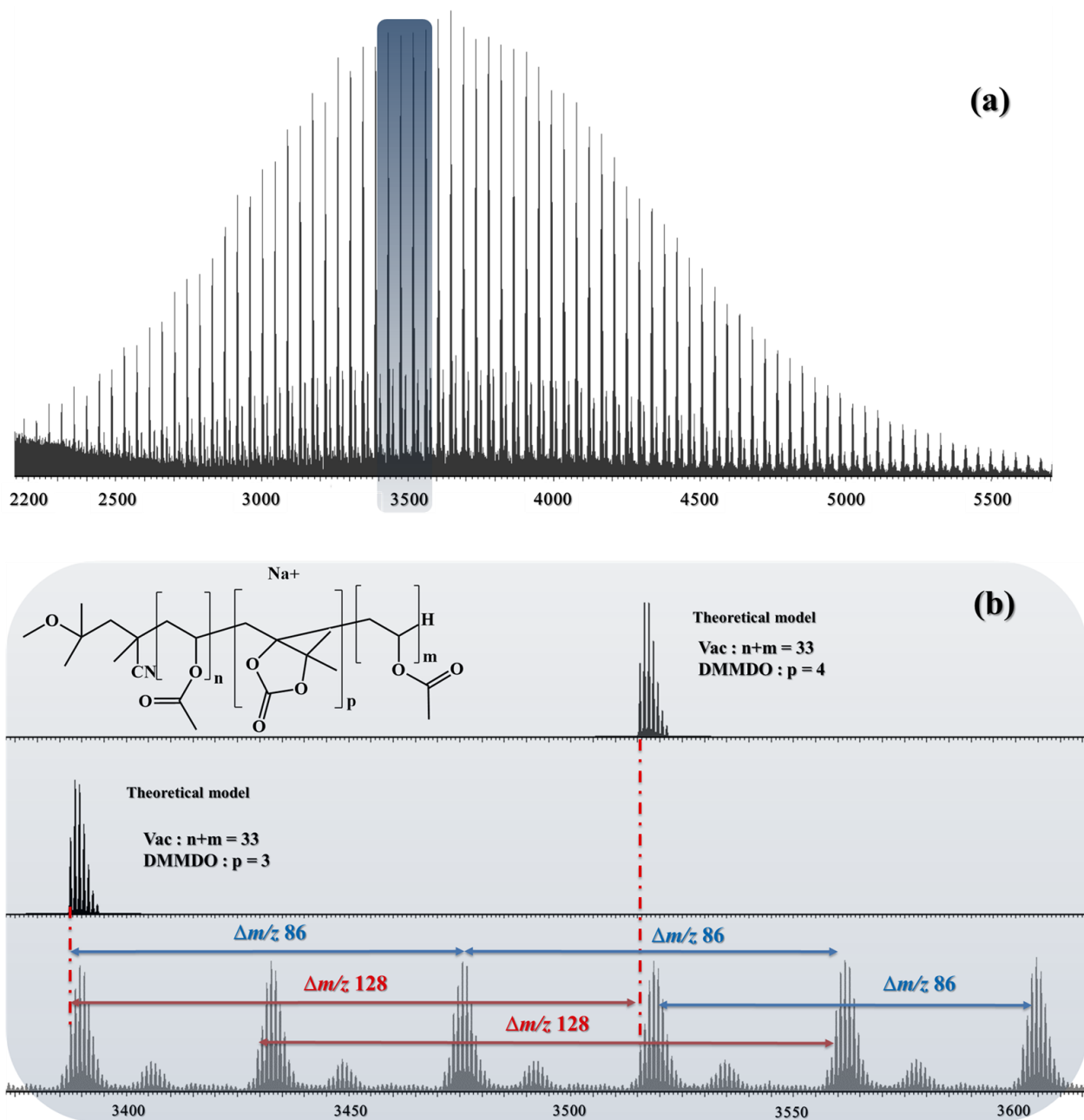
All these analyses are in line with the copolymer structure, thus with the intact cyclic carbonate. The low temperature of CMRP (40 °C) allowed to preserve the cyclic carbonate structure and prevent rROP. This is in line with free radical copolymerisation of DMMDO, favouring rROP at high temperatures (> 120 °C).<sup>24,25</sup> Additionally, a minimal amount of residual cobalt (147 ppm; compared to an initial content of 3,924 ppm) was determined using ICP-OE measurements on a copolymer containing 23 mol% DMMDO (Entry 12, Table S1).

A copolymerisation was then carried out at a higher temperature, 90 °C, under otherwise identical conditions ( $f_{\text{DMMDO}}^0 = 0.25$ ,  $M/R\text{-Co}(\text{acac})_2 = 400$ , for 4 hours) in order to evaluate the impact of the temperature on the copolymer structure. SEC analysis of the copolymer showed a  $M_n$  SEC of

10,200 g.mol<sup>-1</sup> (for a  $M_{n \text{ theo}}$  of 8,100 g.mol<sup>-1</sup>) but with a high dispersity ( $M_w/M_n = 2.61$ ), in line with a loss of control. Despite the expected broadening of the dispersity of the copolymer at this temperature (which was too high for an optimal control of VAc by CMRP)<sup>44</sup>, the <sup>1</sup>H-NMR (Figure S2a) and <sup>13</sup>C-NMR (Figure S2b) spectra were similar to the copolymers formed at 40 °C. At 90°C, rROP was therefore not observed.



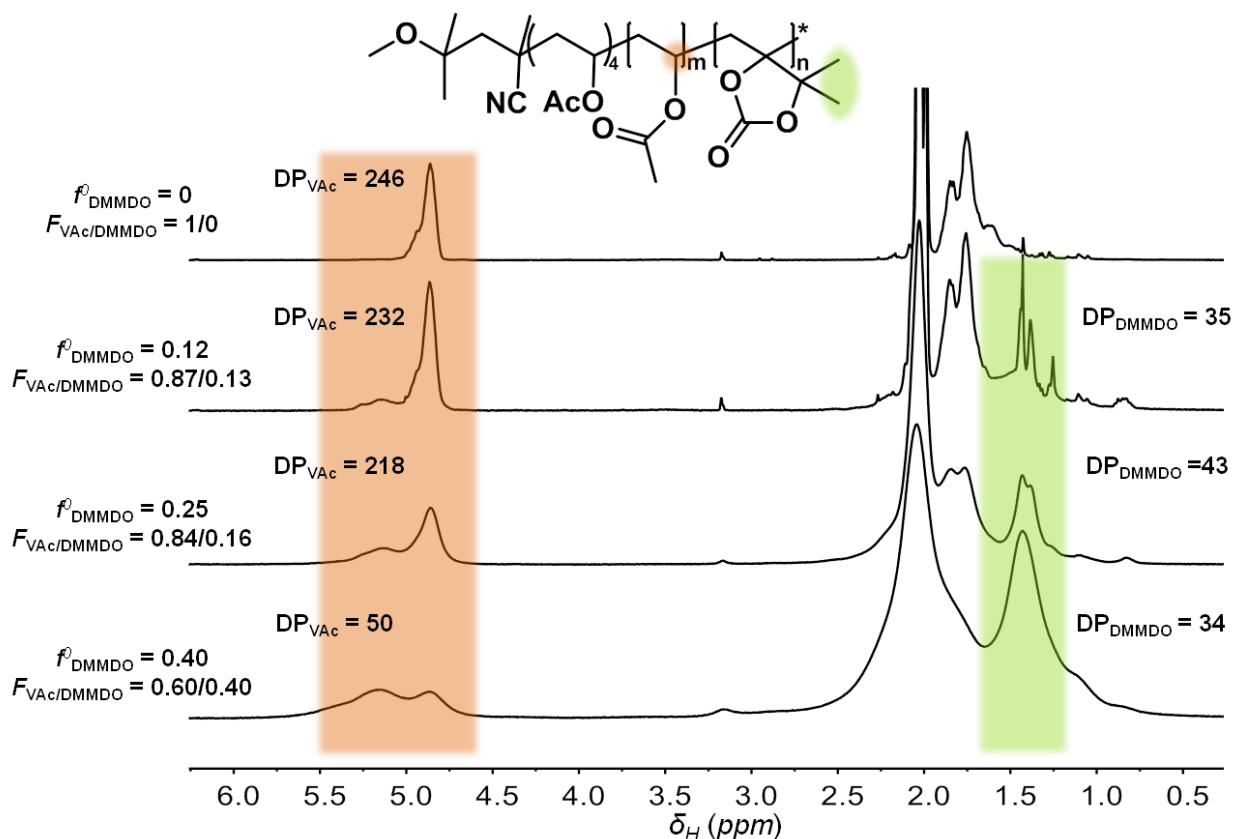
**Figure 2.** a) <sup>1</sup>H-NMR spectrum, b) <sup>13</sup>C-NMR spectrum, c) COSY spectrum and d) HSQC spectrum of a copolymer at 43% conversion containing 16 mol% DMMDO prepared by CMRP at 40 °C (Table 1, Entry 5). NMR spectra taken in CDCl<sub>3</sub> on a 400 MHz spectrometer.



**Figure 3.** MALDI mass spectra recorded for a copolymer containing 16 mol% DMMDO (Table 1, Entry 9) showing a) the global mass spectrum and b) a magnification between  $m/z$  3350 and  $m/z$  3600 and the comparison of the signals with a theoretical model.

Once the structure was elucidated, the composition of the final copolymers was determined by  $^1\text{H-NMR}$  spectroscopy. Figure 2 shows the  $^1\text{H-}$ ,  $^{13}\text{C-NMR}$ , COSY and HSQC spectra of the copolymer prepared using an initial VAc/DMMDO feed ratio of 75/25 after 25 hours of polymerisation (Entry 5, Table 1). The  $^1\text{H-NMR}$  spectrum clearly shows peak **l** at 3.10 ppm, which belongs to the  $\alpha$ -chain end of the copolymers (**l**,  $\text{CH}_3\text{-O}$  at 3.10 ppm) and peaks **d**, **j**, **k** typical of the  $-\text{CH}_3$ ,  $-\text{CH}_2-$  and  $-\text{CH-OAc}$  of VAc, respectively (**d**,  $-\text{CH}_3$  at 1.97 ppm; **j**,  $-\text{CH}_2-$  at 1.74 ppm; **k**,  $-\text{CH-OAc}$  at 4.80 ppm). An additional peak at 1.35 ppm was attributed to the  $-\text{CH}_3$  groups of the CC repeating unit (**h**,  $-\text{CH}_3$  at 1.35 ppm), while the broad signal at 5.10 ppm originates from a deshielded  $-\text{CH-OAc}$  group of VAc next to a DMMDO unit, as confirmed by the HSQC spectrum (**b**,  $-\text{CH-O-}$  at 5.10 ppm). Peaks **c** and **i** in the  $^{13}\text{C-NMR}$  spectrum were attributed to the  $\text{C=O}$  signal of the ester and carbonate of VAc and DMMDO, respectively (**c**,  $\text{C=O}$  at 170 ppm; **i**,  $\text{C=O}$  at 152 ppm). The remaining signals could only be attributed with reference to the HSQC spectrum (Figure 2d) and were in agreement with the proposed chemical structure. Figure 4 presents the  $^1\text{H-NMR}$  spectra of PVAc and P(VAc-co-DMMDO) copolymers prepared by CMRP with feeds ranging from 10 to 40 mol% DMMDO. By increasing the DMMDO in the feed, the integral of the characteristic broad signal, associated with the two  $-\text{CH}_3$  groups of DMMDO repeating units at 1.40 ppm, increased as well as the broad signal at 5.10 ppm that comes from the slightly more deshielded environment of the  $-\text{CH-OAc}$  that is next to a DMMDO repeating unit. Using these characteristic peaks and comparing their relative intensities, the copolymer composition could be determined (see experimental section for details, Figure 4 and Table 1). It should be mentioned, that the difference in DMMDO content of the copolymer compared to the monomer feed observed for entries 3, 4, and 9 (Table 1) is only a few mol%, reaching the limit of the accuracy of NMR spectroscopy, and hence no judgment on the deviation of these entries can be made.





**Figure 4.**  $^1\text{H}$ -NMR spectra of copolymers prepared by CMRP at 40 °C with  $f_{\text{DMMDO}}^0 = 0\text{-}0.4$ . NMR spectra taken in  $\text{CDCl}_3$  on a 400 MHz spectrometer.

Additionally, to better understand the copolymer composition and also to be able to predict the copolymer composition, the reactivity ratios of the two monomers were determined using free radical polymerisation (FRP) at 40 °C. The use of free radical polymerisations was necessary to access a larger variety in compositions, as CMRP is inhibited above 50 mol% DMMDO in the feed. The good agreement of the reactivity ratios values determined by FRP with those obtained by CMRP has been demonstrated in a previous publication<sup>47</sup> and was verified by a few points, as discussed below.

Free radical polymerisations with feeds ranging from 11 to 92 mol% DMMDO were conducted and were quenched at low conversion (<15%) to avoid a composition drift. The polymers were

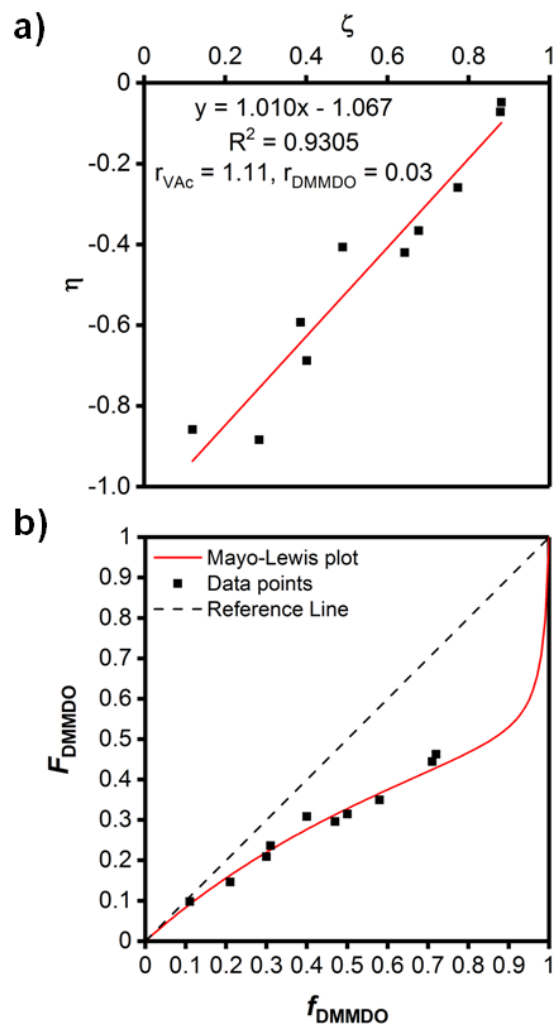
then analysed by  $^1\text{H-NMR}$  spectroscopy to evaluate their composition and the comonomers' conversion, and their macromolecular parameters were determined by SEC (Table S2). For feeds above 72 mol% DMMDO, extremely low polymerisation rates were noted and not enough polymer material was obtained for accurate analysis.

Three compositions ( $F$ ) obtained at specific feeds ( $f$ ) by FRP were verified using CMRP in order to demonstrate that compositions are similar by both processes. The discrepancies of the composition obtained by classical radical polymerisation *versus* controlled radical polymerisation were observed to be within 9 mol% of each other (Table S2, comparison of entries 1, 4 and 5 for FRP with entries 12-14 for CMRP).

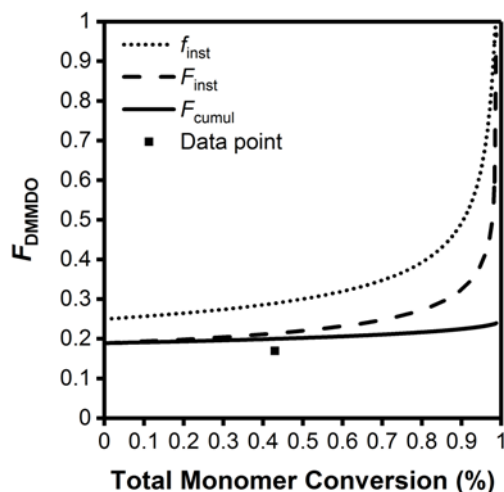
The Kelen-Tüdös (KT) linearisation method was used to determine the reactivity ratios:  $r_{\text{DMMDO}} = 0.03$ ,  $r_{\text{VAc}} = 1.11$  (Figure 5a).<sup>33-35</sup> A reactivity ratio close to 0 for DMMDO highlighted the well-known inability of this monomer to homopolymerise. It also means that during the copolymerisation with VAc, a chain-end DMMDO radical almost always cross-propagates. On the other hand,  $r_{\text{VAc}}$  of 1.11 was obtained for VAc, meaning that such a chain-end radical can add to both monomers without inclination towards one or the other. As a result, a preferential incorporation of VAc into the copolymer was observed and the DMMDO repeat units are isolated within the copolymer backbone. Additionally, the final copolymer composition at different feeds was computed using the Mayo Lewis equation (Figure 5b).

In order to give further insights on the distribution of the comonomer units along the chains, the instantaneous and the cumulative copolymer compositions were predicted on the whole range of monomer conversions through the Skeist equation using the reactivity ratios determined above (see experimental part for detailed equations). Figure 6 shows the evolution of the instantaneous feed ( $f_{\text{inst}}$ ), the copolymer composition ( $F_{\text{inst}}$ ) and the cumulative copolymer composition ( $F_{\text{cumul}}$ ) *versus* the overall comonomer conversion. As an example, we considered an initial DMMDO

molar fraction in the feed ( $f^0_{\text{DMMDO}}$ ) of 0.25 (Entry 5, Table 1). The experimental cumulative copolymer composition, determined by  $^1\text{H}$  NMR spectroscopy at 43% conversion for  $f^0_{\text{DMMDO}} = 0.25$  and represented by a black dot in Figure 6, fitted well with the predicted cumulative composition curve ( $F_{\text{cumul}}$ , full line in Figure 6). Skeist's plot shows that the instantaneous copolymer composition does not change during the polymerisation for conversions below 80 % and for such conversions the DMMDO monomer is homogeneously distributed throughout the polymer chain (Figure 6). As an illustration, a copolymer prepared from a feed of 25 mol% DMMDO at 43% total conversion (Table 1, entry 5) contains on average 218 repeating units of VAc and 43 repeating units of DMMDO. Therefore, there is an average distance of 5 VAc repeating units between two DMMDO ones.



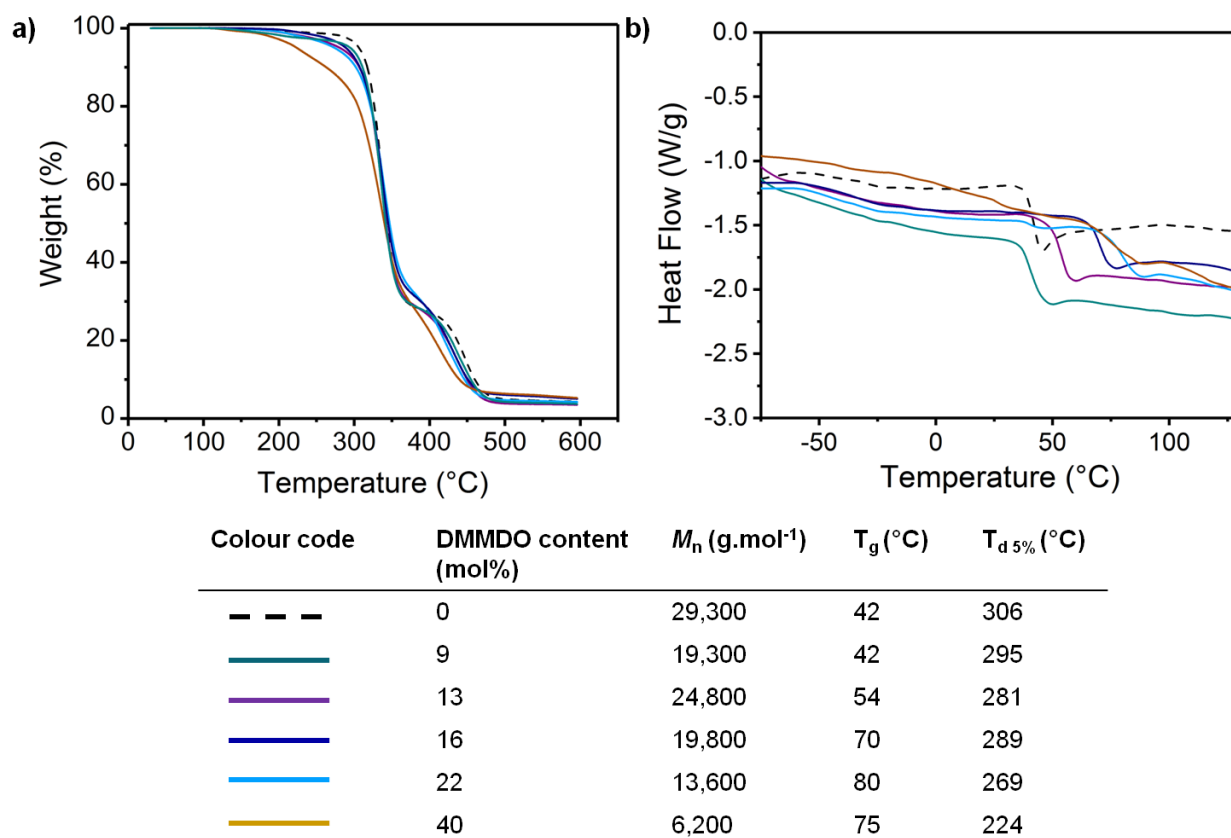
**Figure 5.** a) Kelen-Tüdös linearisation plot ( $r_{VAc} = 1.11$  and  $r_{DMMDO} = 0.03$ ) and b) Mayo-Lewis plot using experimental reactivity ratios.



**Figure 6.** Skeist's plot for a feed of 25 mol% DMMDO of instantaneous reaction composition ( $f_{\text{inst}}$ ), instantaneous copolymer composition ( $F_{\text{inst}}$ ) and cumulative copolymer composition ( $F_{\text{cumul}}$ ) against overall monomer conversion using  $r_{\text{DMMDO}} = 0.03$  and  $r_{\text{VAc}} = 1.11$ . The composition of a copolymer at 43 % conversion containing 16 mol% DMMDO is also plotted (Table 1, Entry 5).

The thermal properties of the produced polymers were then investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). It was observed that the copolymers had a lower degradation temperature than PVAc with a temperature at 5% weight loss ( $T_{\text{d } 5\%}$ ) of 224 to 289 °C versus 306 °C, respectively (Figure 7a). Moreover,  $T_{\text{d } 5\%}$  strongly depends on the copolymer composition. It decreased from 281 °C to 224 °C with increasing DMMDO content in the copolymer. Rapid degradation of the copolymer was observed for all polymers above 300 °C. The glass transition temperatures ( $T_{\text{g}}$ ) of these polymers strongly increased compared to the homopolymer of PVAc, reaching a maximum of 80 °C for polymers containing 22 mol% DMMDO (Figure 7b), which is not unexpected due to the bulky and rigid structure of the DMMDO monomer. The lower  $T_{\text{g}}$  for the copolymer containing 40 mol% DMMDO was

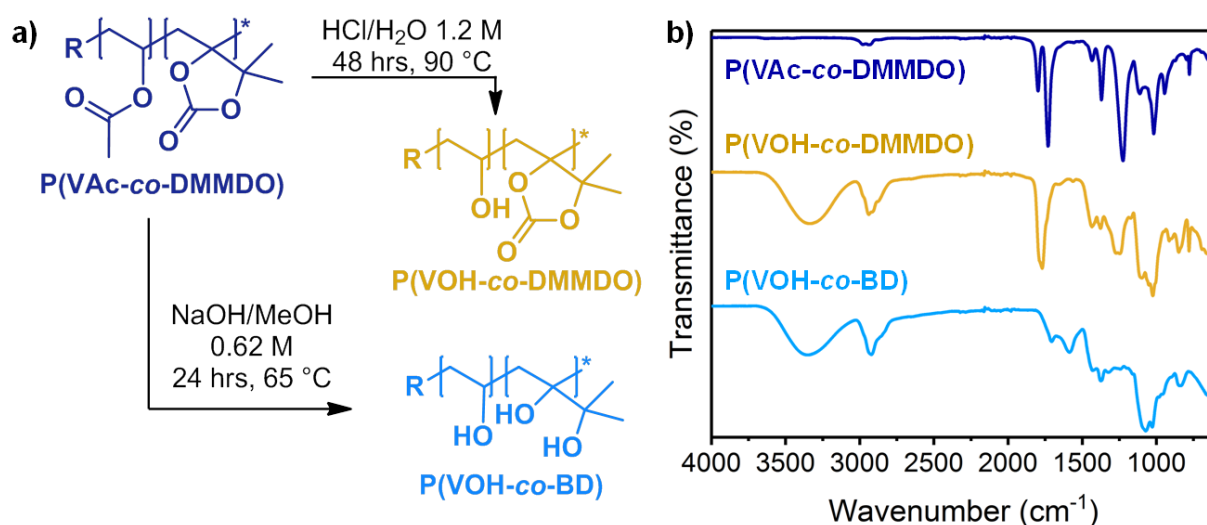
attributed to its lower molar mass compared to the copolymer containing 22 mol%. Overall, the incorporation of the cyclic carbonate in the polymer structure clearly increased the  $T_g$  while decreasing the degradation temperature.



**Figure 7.** a) Thermogravimetric analysis (TGA) curves b) differential scanning calorimetry (DSC) curves of P(VAc-co-DMMDO) of various compositions (Entries 1 and 3-7, Table 1).

**Chemo-selective and complete hydrolysis of P(VAc-co-DMMDO).** The hydrolysis of PVAc is the most common procedure for the synthesis of the highly hydrophilic poly(vinyl alcohol) (PVOH); both acidic<sup>51</sup> and basic<sup>37,52,53</sup> routes are used. However, PVOH presents several drawbacks, of which the main one is its poor solubility at room temperature or at high concentration as the result of its very regular hydrogen-bonding network.<sup>28,54,55</sup> The addition of a

comonomer that is able to disrupt this network has been shown to be an effective way to increase the solubility of PVOH.<sup>39,55–57</sup> Hence the hydrolysis of the copolymers prepared above was very interesting as it would generate chemically modified PVOH. The chemo-selective hydrolysis of the ester groups of the VAc units would yield P(VOH-*co*-DMMDO), thus PVOH with pendant cyclic carbonate functionalities (Figure 8a). In contrast, full methanolysis of both ester groups of VAc units and cyclic carbonates of DMMDO units would provide a PVOH copolymer (P(VOH-*co*-BD)) bearing butane-2,3-diol units (BD; Figure 8a) that are expected to improve the copolymer water solubility compared to unmodified PVOH.



**Figure 8.** a) Acidic hydrolysis and methanolysis conditions of P(VAc<sub>182-*co*</sub>-DMMDO<sub>42</sub>) (19 mol% DMMDO; Entry 10, Table S1) into the corresponding P(VOH<sub>182-*co*</sub>-DMMDO<sub>42</sub>) and P(VOH<sub>182-*co*</sub>-BD<sub>42</sub>), and b) FT-IR spectra of the various copolymers.

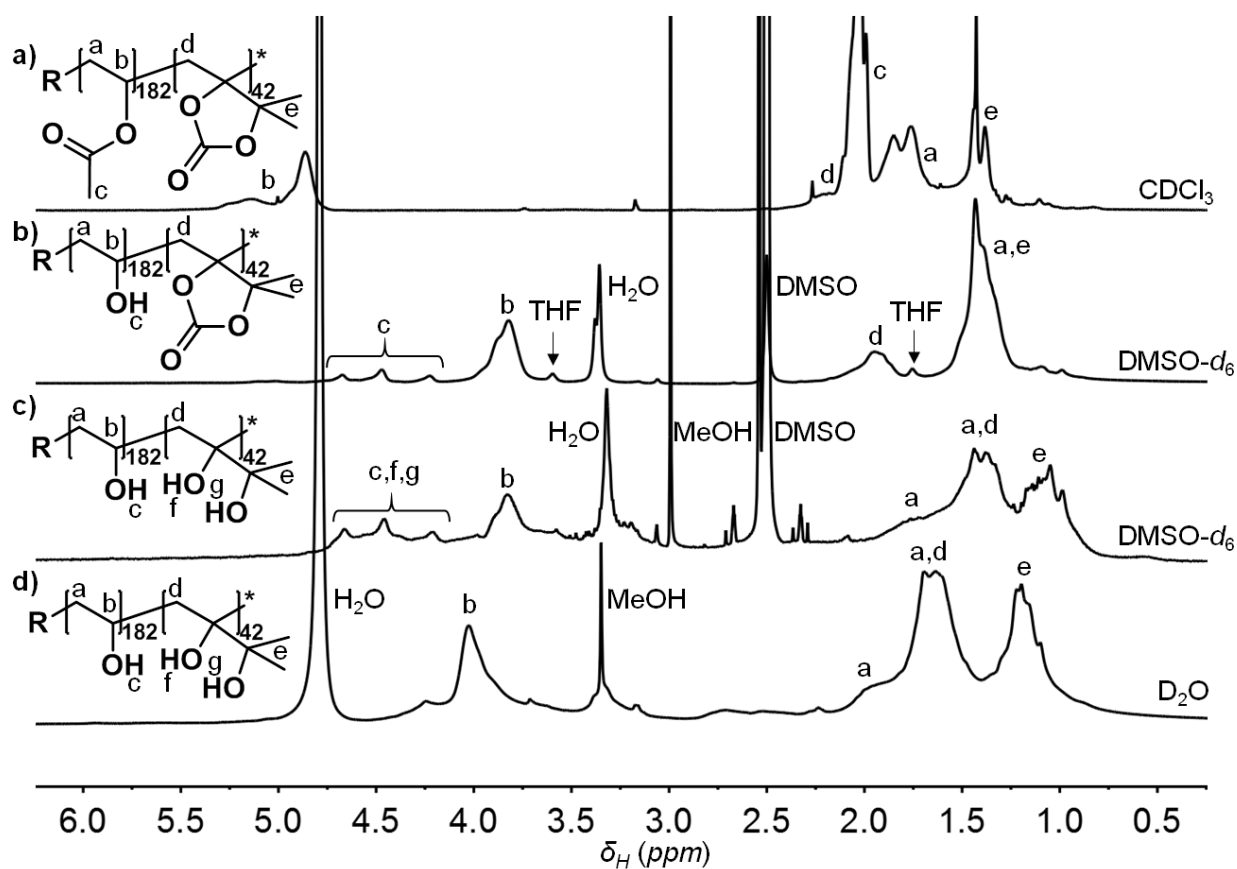
A P(VAc<sub>182-*co*</sub>-DMMDO<sub>42</sub>) copolymer containing 19 mol% DMMDO (Entry 10, Table S1) was subjected to methanolysis and acidic hydrolysis conditions according to previous reports.<sup>43,51,52,56</sup> Under acidic treatment (HCl (1.2 M) in water) at 90 °C for 48h, chemo-selective hydrolysis of

the ester functionality was observed. The  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  analyses of the starting P(VAc-co-DMMDO) copolymer before and after treatment validated the selective hydrolysis (Figures 9 and 10). In the  $^1\text{H-NMR}$  spectra (Figure 9), the disappearance of the signal **b** at 4.79 ppm corresponding to the  $-\underline{\text{CH}}\text{-OAc}$  proton of PVAc (**b**,  $-\underline{\text{CH}}\text{-OAc}$  at 4.79 ppm), and the appearance of the signals typical of P(VOH) (**b**,  $-\underline{\text{CH}}\text{-OH}$  at 3.80 ppm, and **c**,  $-\text{CH}\text{-}\underline{\text{OH}}$  at 4.2-4.7 ppm) confirmed the hydrolysis of PVAc. The presence of signal **d** at 1.97 ppm was in line with the preserved DMMDO units (**d**,  $-\underline{\text{CH}}_2$  at 1.97 ppm). The selective hydrolysis was also highlighted in the  $^{13}\text{C-NMR}$  spectra (Figure 10a and b) through the complete disappearance of the characteristic signal of the ester group at 170 ppm and the preservation of the carbonate signal at 154 ppm. Additional evidence for the successful selective hydrolysis of VAc units was provided by the comparison of infrared spectra of the copolymer before and after treatment, which showed the disappearance of the absorption band of the ester groups at  $1738\text{ cm}^{-1}$ , the appearance of the OH stretching band of PVOH at  $3330\text{ cm}^{-1}$ , and the retention of the cyclic carbonate band at  $1780\text{ cm}^{-1}$  (Figure 8b). Another indication that the hydrolysis was selective to the ester functionalities was obtained by comparing the  $\text{DP}_{\text{DMMDO}}$  before and after hydrolysis. The  $\text{DP}_{\text{DMMDO}}$  before hydrolysis was determined to be 42. Comparing the relative integrals of **b** and **d** (**b**,  $-\underline{\text{CH}}\text{-OH}$  at 3.80 ppm; **d**,  $-\underline{\text{CH}}_2$  at 1.97 ppm; Figure 9b) in P(VOH<sub>182-co</sub>-DMMDO<sub>42</sub>), it was found that the DP after hydrolysis is 44, which was unchanged – within the accuracy that  $^1\text{H-NMR}$  spectroscopy provides – compared to the initial P(VAc<sub>182-co</sub>-DMMDO<sub>42</sub>) (For detailed calculations see experimental part, Figure S3).

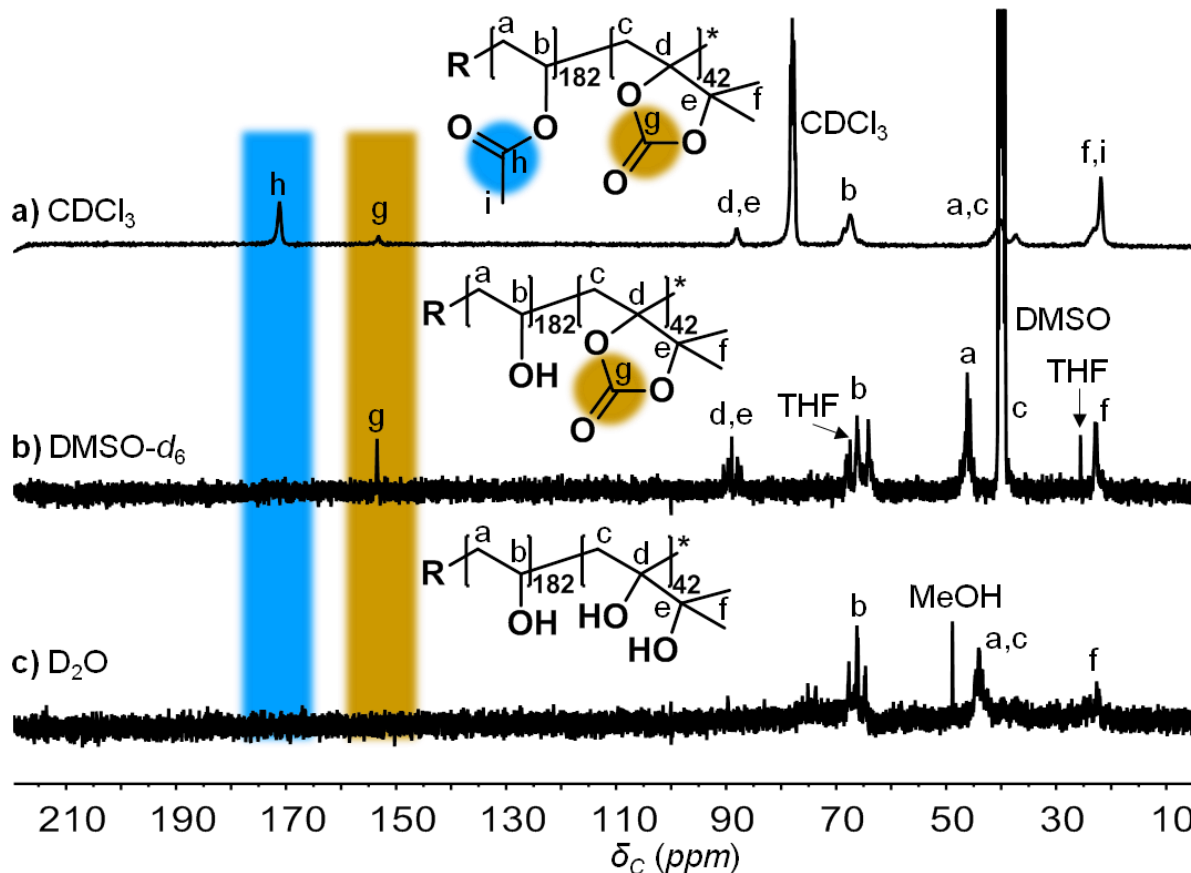
On the other hand, complete methanolysis was observed under basic conditions (NaOH 0.62 M) at  $65\text{ }^\circ\text{C}$  for 24h, as demonstrated by the complete disappearance of the ester and carbonate vibrations in the FT-IR spectrum (Figure 8b), and of the typical ester and carbonate signals in the  $^{13}\text{C-NMR}$  spectrum (Figure 10c). Yet, three weak peaks were observed in the  $^{13}\text{C-NMR}$  spectrum



and were attributed to the  $-\underline{\text{C}}\text{H}_2-$ ,  $-\underline{\text{C}}\text{HOH}-$  and  $-\underline{\text{C}}\text{H}_3$  environments (**a** and **c**,  $-\underline{\text{C}}\text{H}_2-$  at 44 ppm; **b**,  $-\underline{\text{C}}\text{HOH}$  at 66 ppm and **f**,  $-\underline{\text{C}}\text{H}_3$  at 23 ppm), while the tertiary carbon environments **d** and **e** were not observed. In the  $^1\text{H-NMR}$  spectrum (Figure 9c), peaks **d** and **e** shifted upfield, due to the methanolysis of the CC ring, while peak **a** did not change significantly from the selectively hydrolysed copolymer (**d**,  $-\underline{\text{C}}\text{H}_2-$  at 1.25 ppm; **e**,  $-\underline{\text{C}}\text{H}_3$  at 23 ppm; **a**,  $-\underline{\text{C}}\text{H}_2\text{CH-OH}$  at 1.4 ppm). Interestingly, the choice of solvent, in this case DMSO- $d_6$  or  $\text{D}_2\text{O}$ , played an important role on the chemical shift of the peaks in the  $^1\text{H-NMR}$  spectra, as  $\text{D}_2\text{O}$  significantly deshielded the signals possibly because of the increased hydrogen bonding (Figure 9c and d).



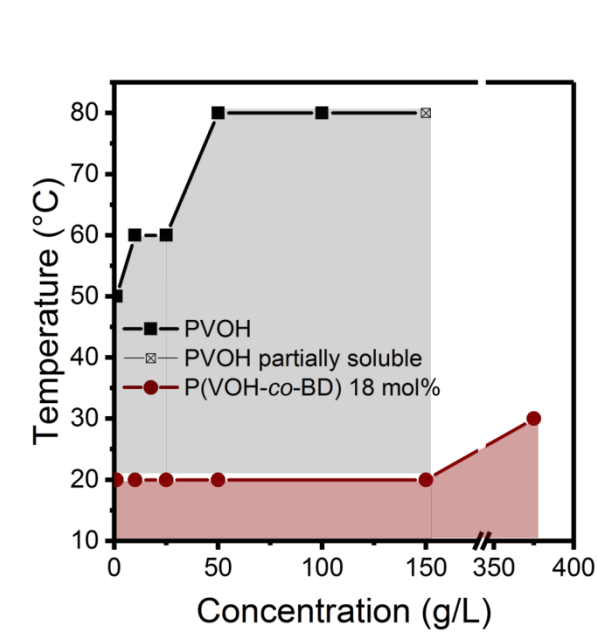
**Figure 9.**  $^1\text{H-NMR}$  spectra of a) P(VAc<sub>182</sub>-co-DMMDO<sub>42</sub>) (19 mol% DMMDO; Table S1, Entry 10) in  $\text{CDCl}_3$ , b) P(VOH<sub>182</sub>-co-DMMDO<sub>42</sub>) in DMSO- $d_6$ , c) P(VOH<sub>182</sub>-co-BD<sub>42</sub>) in DMSO- $d_6$  and d) P(VOH<sub>182</sub>-co-BD<sub>42</sub>) in  $\text{D}_2\text{O}$ . All spectra were recorded on a 400 MHz spectrometer.



**Figure 10.** Overlay of  $^{13}\text{C}$ -NMR spectra of P(VAc<sub>182</sub>-co-DMMDO<sub>42</sub>) (19 mol% DMMDO; Table S1, Entry 10) in  $\text{CDCl}_3$ , P(VOH<sub>182</sub>-co-DMMDO<sub>42</sub>) in  $\text{DMSO}-d_6$  and P(VOH<sub>182</sub>-co-BD<sub>42</sub>) in  $\text{D}_2\text{O}$ . All spectra were recorded on a 400 MHz spectrometer.

The solubility of the fully methanolysed copolymer in 0.5 mL of water was significantly improved when compared to an analogous PVOH prepared by CMRP with a similar DP (DP around 133; Table S3, Entries 1 and 2, Figure 11). While 1 mg of PVOH<sub>134</sub> could only be solubilised at 50 °C, the same amount of P(VOH<sub>108</sub>-co-BD<sub>24</sub>), containing 18 mol% BD units, could be easily solubilised at room temperature. This difference in solubility was further evidenced as the concentration is increased, as the P(VOH<sub>108</sub>-co-BD<sub>24</sub>) copolymer was soluble at a concentration of 375 g/L at 30 °C, while the equivalent PVOH<sub>134</sub> was only partially soluble at a

concentration of 150 g/L at 80°C. The selectively hydrolysed copolymer was not soluble in water.

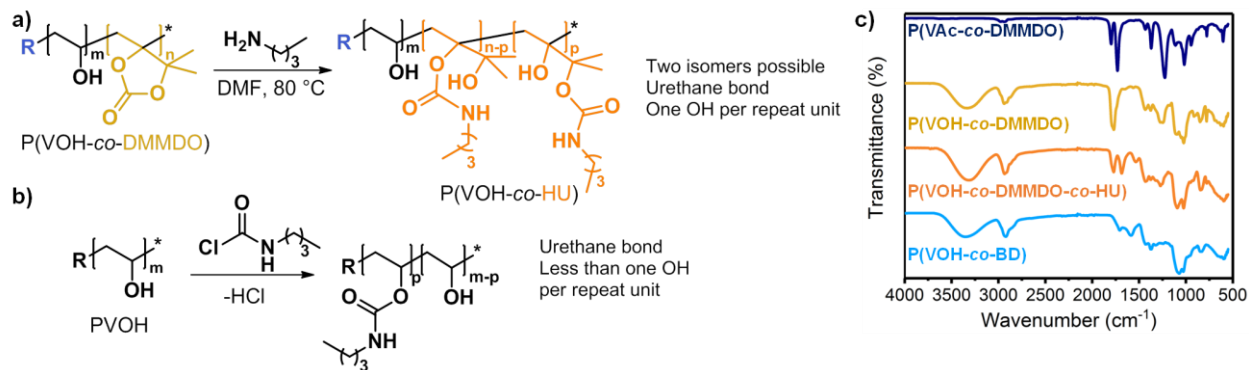


**Figure 11.** Temperature of solubilisation of PVOH<sub>134</sub> and P(VOH<sub>108-co</sub>-BD<sub>24</sub>) in water at different concentrations (Table S4)

### **Post-polymerisation modification of the selectively hydrolysed copolymer (P(VOH-co-DMMDO))**

The selectively hydrolysed copolymer prepared above was of great interest for further post-polymerisation modifications on the cyclic carbonate: a nucleophilic ring opening of the carbonate allows for the functionalisation while keeping an intact backbone (Figure 12a). To achieve a functionalisation with carbamate moieties on an analogous PVOH would result in the loss of an -OH group and thus an unwanted change in the copolymer properties (Figure 12b). Furthermore, highly toxic chloroformates would be necessary for this transformation. As a proof of concept, a P(VOH<sub>149-co</sub>-DMMDO<sub>44</sub>) containing 23 mol% DMMDO (Entry 12, Table S1) was

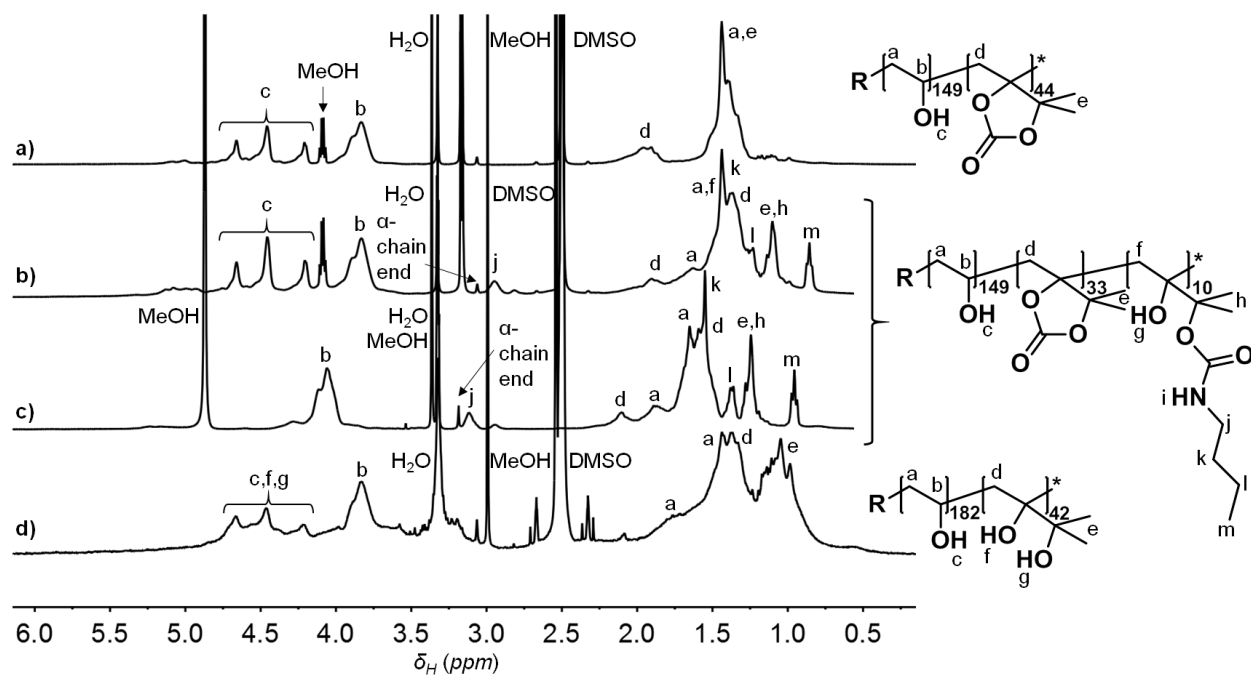
treated with n-butylamine using TBD as a catalyst in DMF at 80°C under anhydrous conditions. In the FT-IR, the characteristic carbonyl absorbance at 1780 cm<sup>-1</sup> decreased in intensity and two further absorbances at 1688 cm<sup>-1</sup> and 1530 cm<sup>-1</sup> were observed (Figure 12c). These were attributed to the C=O stretching of the newly formed urethane bond and the N-H bending, respectively. As the ring-opening can occur on either side of the ring, two possible isomers were expected to be formed (Figure 12a), but cannot be discriminated by NMR analysis (Figure 13b and c). For simplicity, only one of the two possible isomers will be shown from here on. In the <sup>1</sup>H-NMR spectrum, the appearance of peak **m** at 0.87 ppm and peak **j** at 2.97 were characteristic of the  $-\underline{\text{C}}\underline{\text{H}}_3$  group and the  $-\text{N}-\underline{\text{C}}\underline{\text{H}}_2-$  of the butyl urethane functionality, respectively (**j**,  $-\text{N}-\underline{\text{C}}\underline{\text{H}}_2-$  at 2.97 and **m**,  $-\underline{\text{C}}\underline{\text{H}}_3$  at 0.87 ppm). The  $-\underline{\text{N}}\underline{\text{H}}-$  proton was not visible (absence of peak **i**), which is likely to be a result of solvent exchange. The successful functionalisation of the copolymer was also observed in the <sup>13</sup>C-NMR spectrum (Figure S4), which resembled that of P(VOH-co-BD) with peaks **a**, **b**, **c** and **f**, all at the same chemical shifts as for P(VOH-co-BD) (**a** and **c**,  $-\underline{\text{C}}\underline{\text{H}}_2-$  at 46 ppm; **b**,  $-\underline{\text{C}}\underline{\text{H}}\underline{\text{O}}\underline{\text{H}}$  at 66 ppm; **f**,  $-\underline{\text{C}}\underline{\text{H}}_3$  at 25 ppm). However, an additional peak was apparent at 14 ppm, which was attributed to the  $-\underline{\text{C}}\underline{\text{H}}_3$  of the butyl urethane (**p**,  $-\underline{\text{C}}\underline{\text{H}}_3$  at 14 ppm) while no trace of the urethane N-( $\underline{\text{C}}=\underline{\text{O}}$ )-O was observed (absence of peak **l**). With the aid of the HSQC spectrum, two more peaks at 32 and 20 ppm were attributed to the  $-\underline{\text{C}}\underline{\text{H}}_2-$  groups of the butyl urethane group (**n**,  $-\underline{\text{C}}\underline{\text{H}}_2-$  at 32 ppm; **o**,  $-\underline{\text{C}}\underline{\text{H}}_2-$  at 20 ppm). These signals were all supported by the COSY and HSQC spectra (Figure S5). Yet the functionalisation was not complete, as the residual  $-\underline{\text{C}}\underline{\text{H}}_2-$  peak in the <sup>1</sup>H-NMR spectrum (**d**,  $-\underline{\text{C}}\underline{\text{H}}_2-$  at 1.90 ppm; Figure 13b), and the  $\underline{\text{C}}=\underline{\text{O}}$  signal and the  $-\underline{\text{C}}-$  signals in the <sup>13</sup>C-NMR spectrum (**g**,  $\underline{\text{C}}=\underline{\text{O}}$  at 154 ppm; **d** and **e**,  $-\underline{\text{C}}-$  at 89 ppm; Figure S4b) of the intact CC repeating unit were still observed and thus a terpolymer containing vinyl alcohol, DMMDO and hydroxy urethane repeat units (P(VOH-co-DMMDO-co-HU)) was formed.



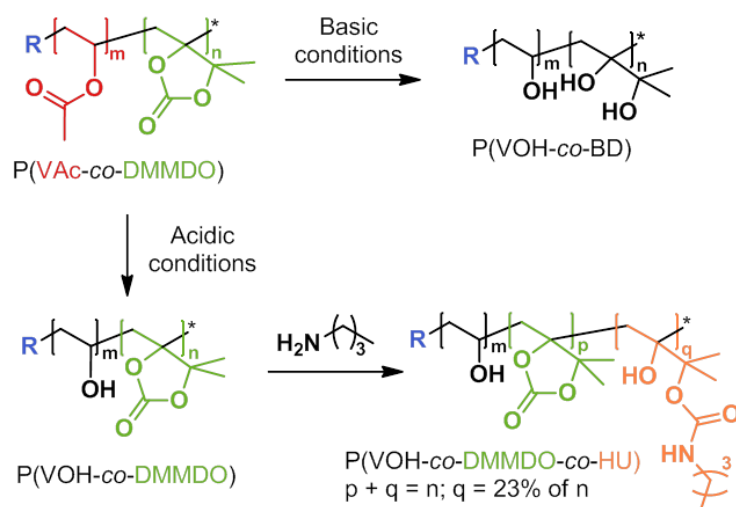
**Figure 12.** Post-modification with butylamine of a) P(VOH-co-DMMDO) to give P(VOH-co-HU), a structure with one –OH unit per repeat unit which is inaccessible with b) PVOH where one less –OH unit is present after modification and c) FT-IR spectra of P(VAc<sub>149</sub>-co-DMMDO<sub>44</sub>), P(VOH<sub>149</sub>-co-DMMDO<sub>44</sub>), P(VOH<sub>149</sub>-co-DMMDO<sub>33</sub>-co-HU<sub>10</sub>) functionalised using dry n-butylamine and P(VOH<sub>182</sub>-co-BD<sub>42</sub>)

Using MeOD-*d*<sub>4</sub> as the solvent for the <sup>1</sup>H-NMR spectroscopy analysis instead of DMSO-*d*<sub>6</sub> shifted the water signals upfield, liberating the –CHOH signal of the VOH (Figure 13b and c). Integrating the –NHCH<sub>2</sub>– peak of the urethane group (3.23 – 3.01 ppm) in the <sup>1</sup>H-NMR spectra recorded in MeOD-*d*<sub>4</sub> and comparing it with the –CHOH integral of the VOH group (4.48 – 3.77 ppm) (see experimental section for calculation details, Figure S6), the degree of functionalisation was estimated to be 23%, which corresponds to 10 urethane repeat units. The unfunctionalised DP<sub>DMMDO</sub> was determined to be 33, which fits with the proposed structure. Interestingly, a slightly lower degree of functionalisation – 16% or DP<sub>HU</sub> = 7 – was observed when wet (thus not pre-dried) n-butylamine was used while no difference in copolymer structure could be identified (Figure S7-S8). The structure of the selectively hydrolysed copolymer was therefore post-modified by the addition of n-butylamine, but further investigations are needed to optimise the reaction conditions and to determine the properties of the obtained copolymers. In summary,

three different copolymer structures were thus accessed from P(VAc-co-DMMDO): P(VOH-co-BD), P(VOH-co-DMMDO) and P(VOH-co-DMMDO-co-HU) (Scheme 3).



**Figure 13.**  $^1\text{H-NMR}$  spectra of a) P(VOH<sub>149</sub>-co-DMMDO<sub>44</sub>) recorded in DMSO- $d_6$ , b) P(VOH<sub>149</sub>-co-DMMDO<sub>33</sub>-co-HU<sub>10</sub>) functionalised using dry n-butylamine, recorded in DMSO- $d_6$ , c) P(VOH<sub>149</sub>-co-DMMDO<sub>33</sub>-co-HU<sub>10</sub>) functionalised using dry n-butylamine, recorded in MeOD- $d_4$  and d) P(VOH<sub>182</sub>-co-BD<sub>42</sub>) recorded in DMSO- $d_6$ . All spectra are taken on a 400 MHz spectrometer.



**Scheme 3.** Starting from a single copolymer, P(VAc-co-DMMDO), three different copolymers were accessed: P(VOH-co-BD), P(VOH-co-DMMDO) and P(VOH-co-DMMDO-co-HU).

## Conclusion

For the first time, a CO<sub>2</sub>-based  $\alpha$ -alkylidene cyclic carbonate (DMMDO) was statistically copolymerised with vinyl acetate (VAc) in a controlled manner *via* CMRP under mild experimental conditions. Good control over the macromolecular characteristics was observed while the carbonate rings remained intact. The distribution of DMMDO repeat units within the copolymer chains was established using the Skeist model after the determination of the reactivity ratios of the comonomers. For a feed of 25 mol% DMMDO and conversions below 80%, it was observed that DMMDO was homogeneously distributed along the chain. Hydrolysis of both the pendant esters and carbonate groups of the P(VAc-co-DMMDO) copolymer gave PVOH-like copolymers with improved water solubility as compared to unmodified PVOH of a similar degree of polymerisation. The preparation of PVOH copolymers with pendant cyclic carbonate groups was possible by chemo-selective hydrolysis of the acetate groups. These functional copolymers were then post-modified *via* the nucleophilic ring opening of the carbonate ring with butyl amine

leading to PVOH polymers with grafted side-chains. In contrast to the classical PVOH functionalisation methods relying on the transformation of the pendant hydroxyl groups, the present strategy afforded the advantage of preserving one hydroxyl group per repeat unit. The precise copolymerisation of VAc with CO<sub>2</sub>-sourced five-membered cyclic carbonate bearing an exomethylene moiety is therefore a powerful tool for the synthesis of new variants of poly(vinyl alcohol)-based copolymers, whose properties have now to be investigated.

### **Supporting Information.**

Supporting tables (Tables S1-S4 and figures (Figures S1-S8) are in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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