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# **Cobalt-Mediated Radical Copolymerization of Vinylidene fluoride and 2,3,3,3-Trifluoroprop-1-ene**

*Panagiotis G. Falireas\* and Bruno Ameduri\**

ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France.

\*Corresponding Authors: E-mail: bruno.ameduri@enscm.fr (B. Améduri)

E-mail: pfalireas@uliege.be (P.Falireas)

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# Cobalt-Mediated Radical Copolymerization of Vinylidene fluoride and 2,3,3,3-Trifluoroprop-1-ene

*Panagiotis G. Falireas\* and Bruno Ameduri\**

ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France.

\*Corresponding Authors: E-mail: bruno.ameduri@enscm.fr (B. Améduri)

E-mail: pfalireas@uliege.be (P.Falireas)

## Abstract

New copolymers based on vinylidene fluoride (VDF) and 2,3,3,3-tetrafluoroprop-1-ene (1234yf) were synthesized by organometallic-mediated radical copolymerization (OMRcP) using the combination of bis(*tert*-butylcyclohexyl) peroxydicarbonate initiator and bis(acetylacetonato)cobalt(II), (Co(acac)<sub>2</sub>) as a controlling agent. Kinetics studies of the copolymerization of the fluoroalkenes copolymers were monitored by GPC and <sup>19</sup>F NMR with molar masses up to 12,200 g/mol and dispersities (*M<sub>w</sub>/M<sub>n</sub>*) ranging from 1.33 to 1.47. Such a OMRcP behaves as a controlled copolymerization, evidenced by the molar mass of the resulting copolymers-monomer conversion linear relationship. The reactivity ratios, *r<sub>i</sub>*, of both comonomers were determined by using the Finemann-Ross and Kelen-Tüdös fitting model leading to *r<sub>VDF</sub>* = 0.384 ± 0.013, *r<sub>1234yf</sub>* = 2.147 ± 0.129 at 60 °C showing a lower reactivity of VDF to be integrated in the copolymer to a greater extent leads to the production of gradient or pseudo-diblock copolymers.

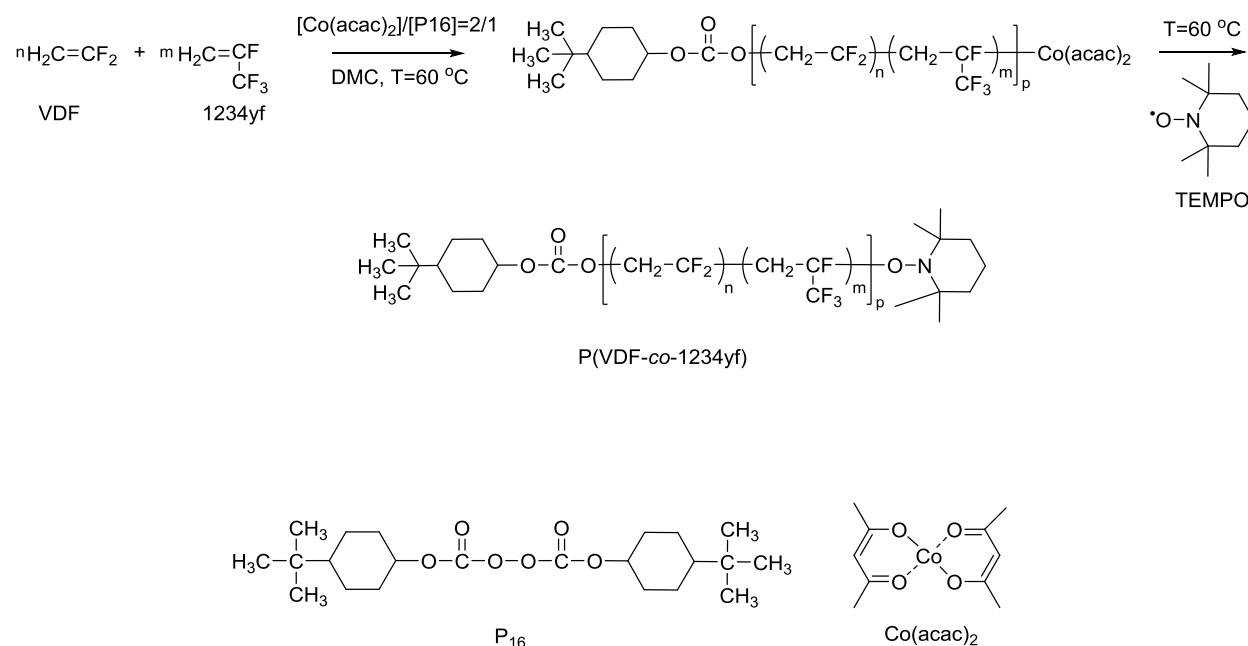
## Introduction

Fluoropolymers are outstanding specialty polymers which exhibit remarkable properties for High Tech applications.<sup>1-4</sup> Most fluorinated homopolymers display a high crystallinity rate (higher than 95% for PTFE) that makes them insoluble in many common organic solvents and further induce energetic processing cost to melt or sinter them.<sup>5</sup> Thus, copolymerizing of fluoroalkenes overcome these limitations as well as enabling better solution characterization. Actually, copolymers of vinylidene fluoride (VDF) have led to many studies and patents.<sup>6, 7 8</sup> Among all VDF comonomers, 2,3,3,3-trifluoropropene, HFO-1234yf ( $\text{CF}_3\text{CF}=\text{CH}_2$ ) is a valuable example of HFO class because it is a low-global warming potential ( $\text{GWP}_{100\text{yrs}} < 1$ ), a Montreal Protocole-regulated substance with high  $\text{CO}_2$ -eq emissions, used in mobile air conditioning.<sup>9-11</sup> Indeed, a few radical copolymerizations of VDF with 1234yf have been reported, either by conventional radical copolymerization<sup>12-14</sup> or under reversible deactivation radical copolymerizations (RDRP), either by iodine transfer copolymerization<sup>15</sup> or RAFT.<sup>16</sup> However, to the best of our knowledge, though VDF has been successfully polymerized by Cobalt mediated radical polymerization (CMRP),<sup>17, 18</sup> though that technique can be well applied on the copolymerization of vinyl acetate (VAc),<sup>19</sup> no study has been achieved on the CMR copolymerization of VDF with 1234yf. Wang et al.<sup>20</sup> reported the CMR copolymerization of chlorotrifluoroethylene (CTFE) with VAc initiated by AIBN in the presence of bis(acetylacetonato)cobalt(II),  $\text{Co}(\text{acac})_2$ , as a controlling agent. Though both molar masses and molar compositions of the resulting copolymers could be “controlled”,  $\bar{D}$  values of the resulting copolymers were high ( $\sim 1.57$ ). Hence, the objective of this present study aims at copolymerizing VDF with 1234yf in controlled conditions by simply using a peroxycarbonate initiator and  $\text{Co}(\text{acac})_2$  as a mediated compound to favor the control of such a reaction. Recently, the current authors have investigated and optimized the polymerization conditions of OMRP of VDF by redox initiation initiated by bis(*tert*-butylcyclohexyl) peroxydicarbonate (P16) and  $\text{Co}(\text{acac})_2$  as a controlling agent.<sup>17</sup> All the polymerizations were carried out in dimethyl carbonate (DMC), a suitable solvent for PVDF oligomers that also exhibits fast rate of VDF polymerization.<sup>21</sup> By applying the same conditions, we investigated the copolymerization of VDF with 1234yf (Scheme 1). The results indicate that the process has the features of a controlled radical polymerization.

## Results and discussion

### Copolymerization of VDF with 1234yf

Recently, we proved that VDF could homopolymerize by OMRP by redox initiation using the combination of P16 and Co(acac)<sub>2</sub>. The best control of the polymerization was found under optimized conditions ([P16]<sub>0</sub>/[Co(acac)<sub>2</sub>]<sub>0</sub> = 2/1, T= 60 °C), leading to PVDF homopolymers with low dispersities (*D*<1.35).<sup>17</sup> Based on the same conditions, we performed the copolymerization of VDF with 1234yf (Scheme 1).

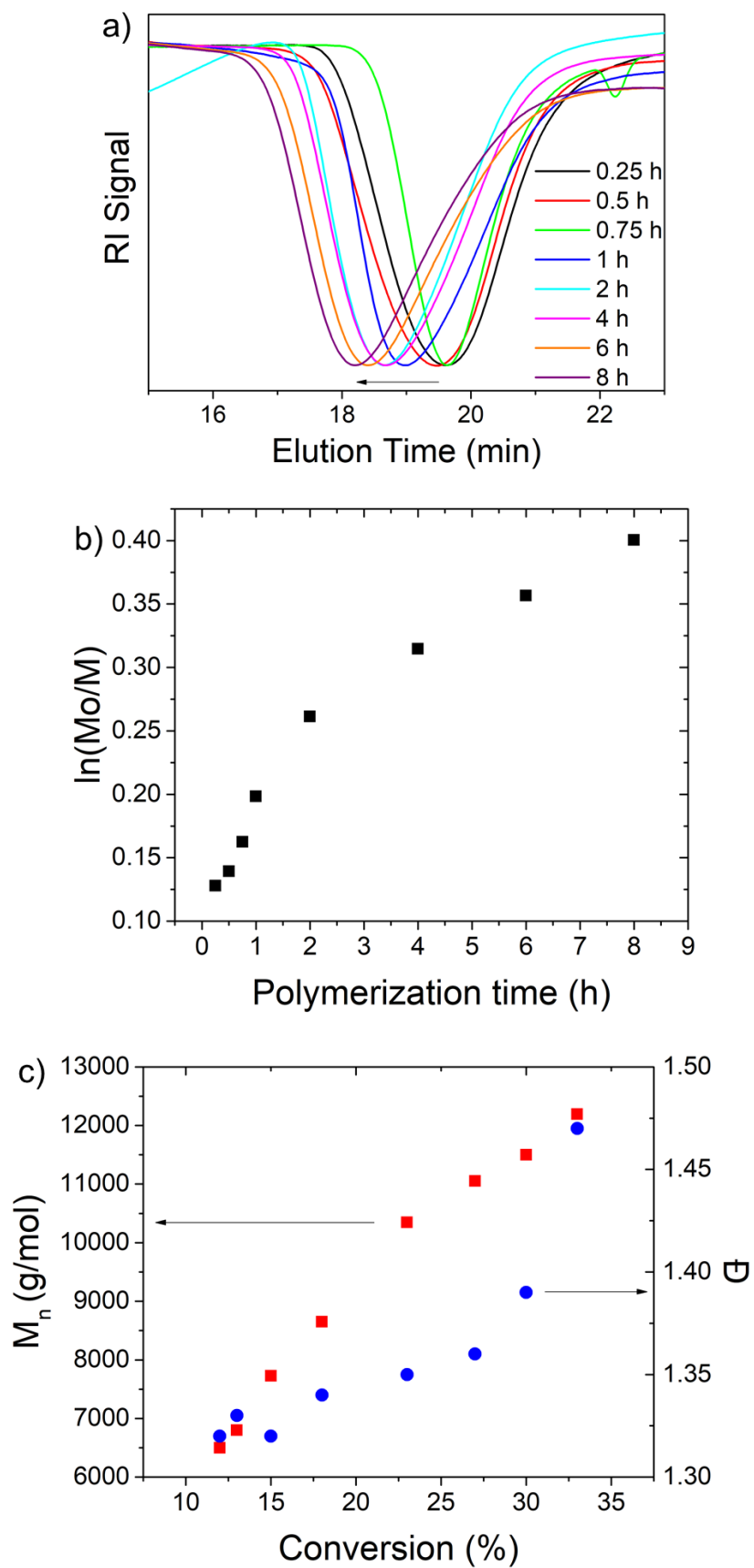


**Scheme 1.** Preparation of P(VDF-co-1234yf) copolymers by OMRP mediated by Co(acac)<sub>2</sub> and initiated by bis(*tert*-butylcyclohexyl) peroxydicarbonate (P16).

In order to get a deeper insight at the copolymerization of VDF with 1234yf, a kinetic study was performed covering the whole conversion of polymerization. Therefore, single point experiments (ranging from 0.25 h to 16 h) were carried out. All copolymerizations were conducted under similar conditions, ([VDF]<sub>0</sub>/[1234yf]<sub>0</sub>/[P16]<sub>0</sub>/[Co(acac)<sub>2</sub>]<sub>0</sub>=80/20/2/1 at 60 °C in DMC and were monitored by <sup>19</sup>F NMR (Figure S2) and GPC measurements equipped with a refractive index detector (Figure 1a). At this point it should be stressed that in order to prevent unfavorable chain terminations all the polymerization was quenched by TEMPO which

according to the literature plays the role of radical scavenger by displacing the covalently bonded  $\text{Co}(\text{acac})_2$  moiety from the propagating active chains.<sup>22</sup>

The GPC eluograms of the synthesized copolymers exhibited negative refractive index signals since the refractive index increment of PVDF in DMF is negative.<sup>23-25</sup> Their profile displayed unimodal distributions showing no sign of coupling reactions and they significantly shifted toward lower elution times throughout the polymerization. Figure 1b illustrates the evolution of  $M_n$  and  $\bar{D}$  versus monomer conversion where the linear relationship between molar mass and conversion indicates that the chain growth is indeed controlled. At the same time dispersities increased progressively from 1.33 to 1.47.



**Figure 1.** Plots of a) GPC eluograms for the VDF/1234yf copolymerization via OMRcP, b)  $\ln([M]_0/[M])$  vs polymerization time and c) evolution of  $M_n$  and  $\bar{D}$  vs the comonomer conversions. Conditions  $([VDF]_0/[1234yf]_0/[P16]_0/[Co(acac)_2]_0=80/20/2/1$  at  $T=60$  °C

Semilogarithmic kinetic plot exhibited two different regimes (Figure 1b). Initially, a fast polymerization was observed without any sign of induction period which is expected for a redox initiating system.<sup>26</sup> The copolymerization proceeded at a fast rate for 1 h, then it slowly decreased until it terminated after 8 h where the conversion reached 33%. Similar polymerization kinetics were found for homopolymerization of VDF by OMRP performed under the same conditions, where the change of polymerization rate was retarded after 2h probably due to limited solubility of PVFD in DMC at 60 °C.<sup>17, 18</sup>

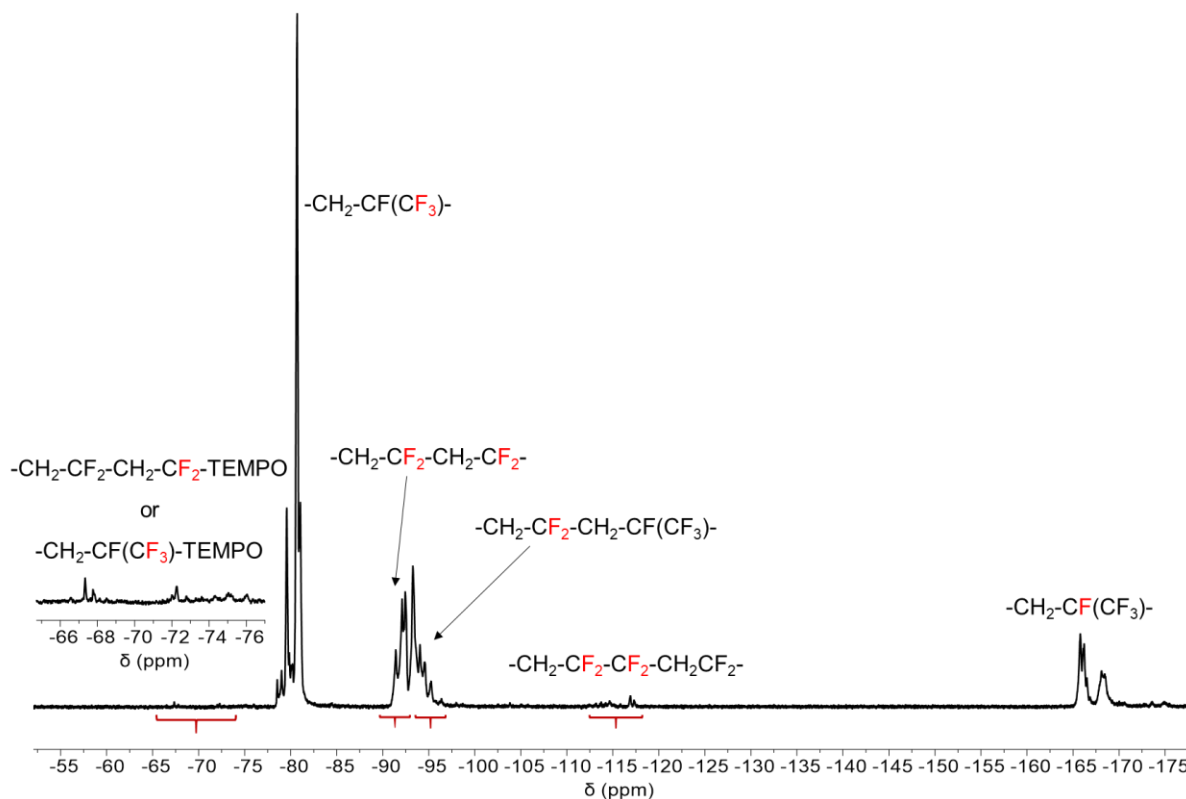
**Table 1.** Results on the kinetics of the copolymerization of VDF with 1234yf via OMRP. Conditions  $([VDF]_0/[1234yf]_0/[P16]_0/[Co(acac)_2]_0=80/20/2/1$  at  $T=60$  °C

Entry	Polymerization time (h)	Conv. (%) <sup>a</sup>	$M_n$ (g/mol) <sup>b</sup>	$\bar{D}$ <sup>b</sup>
1	0.25	12	6500	1.33
2	0.5	13	6800	1.16
3	0.75	15	7700	1.32
4	1	18	8600	1.34
5	2	26	10300	1.29
6	4	27	11000	1.36
7	6	30	11500	1.39
8	8	33	12200	1.47

<sup>a</sup> The conversion was calculated gravimetrically, <sup>b</sup> Number average molar mass and dispersity of the copolymers measured by GPC relative to poly(methyl methacrylate) standards in DMF at 40 °C.

By means of <sup>19</sup>F NMR spectroscopy and based on previously reported studies, it was possible to thoroughly characterize the P(VDF-co-1234yf) synthesized by OMRcP after quenching with TEMPO and purification.



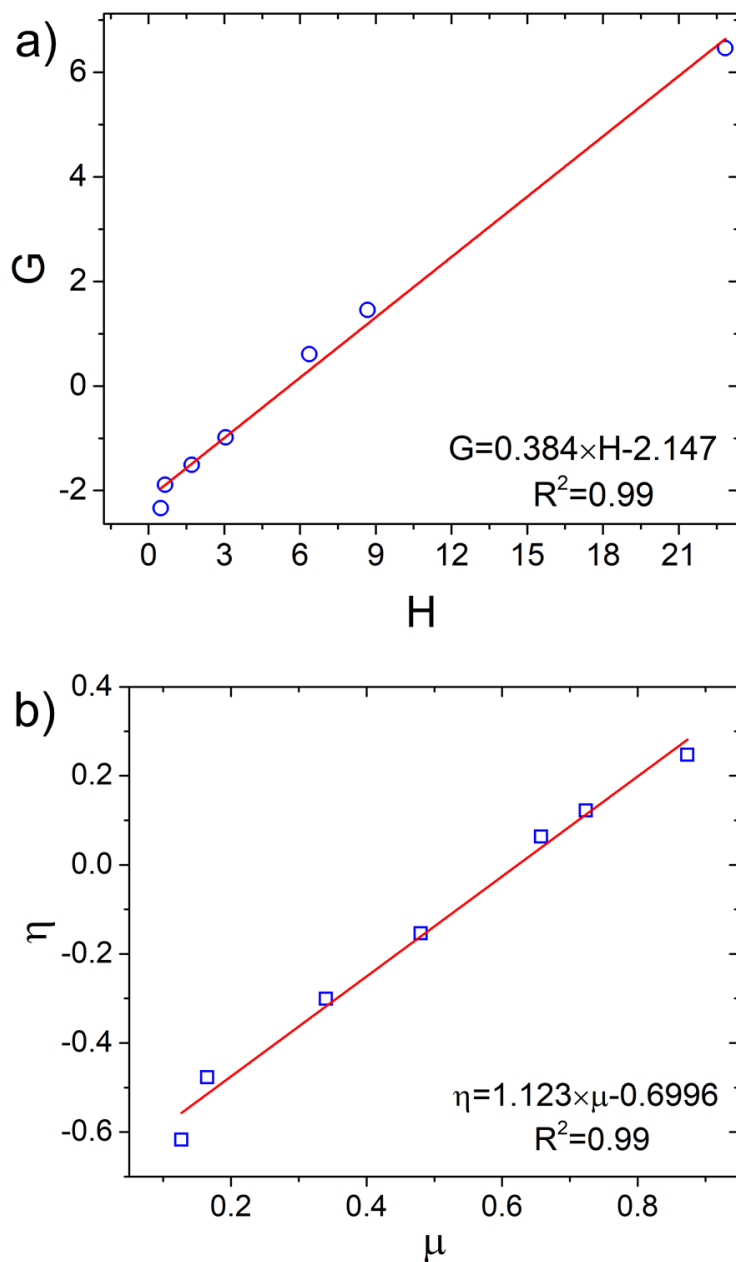


**Figure 2.**  $^{19}\text{F}$  NMR spectrum recorded in  $(\text{CD}_3)_2\text{CO}$  of P(VDF-*co*-1234yf) copolymer synthesized via OMRP at 60 °C (Table 1, Entry 8).

The  $^{19}\text{F}$  NMR spectrum of P(VDF-*co*-1234yf) terminated at 8 h (Table 1, Entry 8) clearly displays a number of characteristic signals attributed to both comonomers: The trifluoromethyl and tertiary fluorine groups of 1234yf in the  $-\text{CH}_2-\text{CF}_2-\text{CH}_2-\text{CF}(\text{CF}_3)-$  dyads of the copolymer are assigned from -78 to -82 ppm and in the -164 to -169 ppm range, respectively. The peaks from -90.6 to -95.4 ppm corresponds to the normal or Head-to-Tail (H-T) VDF-VDF dyads ( $-\text{CH}_2-\text{CF}_2-\text{CH}_2-\text{CF}_2-$ ) in the PVDF chains, while those at -114.6 and -116.9 ppm are attributed to the reverse or Head-to-Head (H-H) VDF-VDF dyads ( $-\text{CH}_2-\text{CF}_2-\text{CF}_2-\text{CH}_2-$ ).<sup>6, 7, 23, 25</sup> Signals from -95.4 to -92.7 ppm are assigned to  $\text{CH}_2-\text{CF}_2-\text{CH}_2-\text{CF}(\text{CF}_3)-$ . Finally, closer inspection in regime between from -66 to -76 ppm revealed the presence of series of peaks which could be attributed to fluorine groups of VDF or 1234yf adjacent to TEMPO end groups.<sup>17, 18</sup>

Additionally, the monomers reactivity ratios of the copolymers prepared by OMRcP were determined via the correlation of the copolymer monomer feed composition relationship. Therefore, a series of seven P(VDF-*co*-1234yf) copolymers was carried out by OMRcP from

initial [VDF]<sub>0</sub>/[1234yf]<sub>0</sub> molar ratios ranging from 90/10 to 16/84 in DMC at 60 °C using a predetermined amount of P16 and Co(acac)<sub>2</sub> which molar ratio was always maintained 2/1. The copolymer conversion was limited to less than 10-15 % to minimize the drift of copolymer makeup. The molar fraction of VDF contained in the copolymer was assessed from <sup>19</sup>F-NMR spectra based on equation 1 (Figure S1, Table S1). It is obvious from the above analysis that the mole fraction of VDF in the copolymers is lower than in the feed ( $f_{\text{VDF}} > F_{\text{VDF}}$ ). This result clearly indicates that there is a significant difference in the reactivity ratios between the fluoromonomers. The reactivity ratios of VDF and 1234yf were determined by applying the Fineman-Ross<sup>27</sup> (Figure 2a) and the Kelen-Tüdös<sup>28</sup> (Figure 2b) approaches. It is clear that regardless of the method chosen to estimate the reactivity ratios, the obtained data is rather similar in each case (Table 2). Specifically, the reactivity ratios are equal to  $r_{\text{vdf}}=0.384 \pm 0.013$ ,  $r_{1234\text{yf}}=2.147 \pm 0.129$  at 60 °C. As can be concluded from the calculations, the reactivity ratio of 1234yf is in every case, significantly higher than that of VDF. The latter signifies that VDF propagation is not preferred in contrast to VDF and 1234yf con-propagation while on the other hand, 1234yf prefers to undergo a homopolymerization rather than a copolymerization. Additionally, the product of the reactivity ratios for the VDF/1234yf copolymerization ( $(r_{\text{vdf}} \times r_{1234\text{yf}}) = 0.8$ ) is close to 1, indicating a slight deviation from random polymerization kinetics and the formation of gradient copolymers of P(VDF-*co*-1234yf). These results are in agreement with those of the literature on previous studies on P(VDF-*co*-1234yf) copolymers synthesized by iodine transfer polymerization and free radical polymerization where VDF is frequently reported as a less reactive monomer in copolymerization procedures.<sup>13, 15</sup>



**Figure 3.** Determination of reactivity ratios for the CMRP of VDF and 1234yf by (a) Fineman-Ross and (b) Kelen-Tüdös models by OMRcP mediated by  $\text{Co}(\text{acac})_2$  and initiated by bis(*tert*-butylcyclohexyl) peroxydicarbonate (P16).

**Table 2.** Reactivity ratios of VDF and 1234yf determined at 60 °C in DMC using initiated by P16 in the presence of  $\text{Co}(\text{acac})_2$ .

Method	VDF/1234yf
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Finemann-Ross	$r_{\text{vdf}}=0.384 \pm 0.013, r_{1234\text{yf}}=2.147 \pm 0.129$
Kelen-Tüdös	$r_{\text{vdf}}=0.434 \pm 0.054, r_{1234\text{yf}}= 2.285 \pm 0.054$

## Conclusions

For the first time, the OMR copolymerization of VDF and 1234yf initiated by the presence of P16 using  $\text{Co}(\text{acac})_2$  as a controlling agent was successfully conducted. Polymerization kinetics was found to lead to acceptable control under optimized conditions ( $[\text{P16}]_0/[\text{Co}(\text{acac})_2]_0 = 2/1$ ,  $T = 60\text{ }^\circ\text{C}$ ), leading to  $\text{P}(\text{VDF-co-1234yf})$  copolymers with relatively low dispersities ( $D < 1.47$ ) until conversion up to 33%. The molar masses, determined by GPC, of the copolymers increased linearly with the copolymer conversions. Moreover, a linear relationship between  $\ln([M]_0/[M])$  and the polymerization time was found. The reactivity ratios of both comonomers were calculated based on Fineman-Ross and Kelen-Tüdös models where similar ratios were obtained in both cases. The monomers reactivity ratios which were found was ( $r_{\text{vdf}}=0.384 \pm 0.013, r_{1234\text{yf}}=2.147 \pm 0.129$  at  $60\text{ }^\circ\text{C}$ ) denoting that 1234yf is more reactive than VDF, thus likely favouring the formation of gradient copolymers. The above results demonstrate that  $\text{Co}(\text{acac})_2$ -mediated controlled radical copolymerization of VDF and 1234yf initiated by P16 is feasible. Finally, future work will look more closely into further optimization of this synthetic strategy which could open the route towards the synthesis of well-defined block terpolymers that will offer the desired combination of properties for advanced applications.

## Acknowledgments

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## GRAPHICAL ABSTRACT

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