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# **Ferrocene/ferrocenium Redox shuttling: peroxide decomposition catalysis applied to vinyl monomers polymerization under suspension conditions**

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## **Abstract**

Ascorbic acid derivatives in combination with ferrocenyl-based activators in catalytic amounts, referred to as kickers, are described as powerful redox systems to promote the decomposition of organic peroxides into radicals for the polymerization of vinyl monomers under suspension conditions. According to the nature of both the vinylic monomer and the peroxide, the initial polymerization rates can be improved by a factor up to 8. In the presence of ferrocene/ascorbyl palmitate kicker, the overall polymerization time of VC was reduced from 3 to 2h under industrial conditions. However, crusting during polymerization as well as yellowing of PVC upon thermal tests were observed. The first problem was solved by changing the surfactant, while optimizing the injection mode of the kicker improved the efficiency of the process without affecting the quality of the resulting PVC. This study demonstrates the effectiveness of ferrocene-based kickers in improving the polymerization of vinyl monomers under suspension conditions.

## **Keywords**

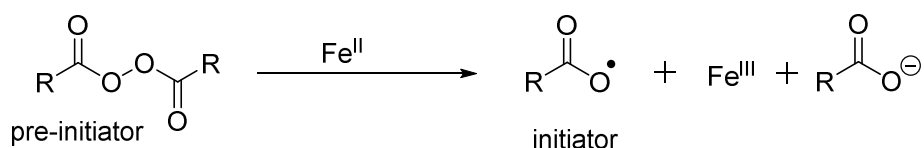
PVC, suspension polymerization, energy efficiency, vinyl monomers, redox catalysis, radical polymerization, peroxide decomposition

## **Introduction**

Free radical polymerization of vinyl monomers is one of the most important and largest synthetic methods for the production of commonly used vinyl polymers. Among these, 40 to 45% of all industrial polymers are manufactured, including poly(methyl methacrylate) (PMMA), polyvinyl acetate (PVAc) and poly(vinyl chloride) (PVC) [1,2]. Moreover, the industrial production of PVC is mainly carried out by the process of radical suspension polymerization, representing around 75% of the total PVC manufactured [3,4].

In general, the radical polymerization starts in the presence of what is called an initiator (typically a free radical), which usually results from the thermal decomposition of a molecule referred to as a pre-initiator like peroxide compound. Promoting peroxide decomposition for radical reactions, and in particular vinyl monomer polymerizations, is an ongoing topic of

interest aimed at improving the initiation step, resulting in an overall enhancement of the reaction rates. This has been studied and applied for several decades and usually involves the use of redox systems to react with peroxide, in addition to the thermal decomposition. In most cases, organic or inorganic reductants are added in stoichiometric amounts *vs.* the peroxide [5], some example being ascorbic acid (AA) and its esters derivatives. As early examples, the use of AA in combination with *tert*-butyl perbenzoate has been described, which allows the homogeneous polymerization of vinyl acetate in alcoholic medium [6] or that of 6-O-palmitoyl-*L*-ascorbic acid (PAA) in bulk or suspension polymerization of vinyl chloride with methyl ethyl ketone peroxide [7] or *t*-butyl peroxyoctoate [8]. Among the inorganic reductants, iron(II) carboxylates have been shown in the early sixties to be efficient for VCM and vinyl acetate (VAc) polymerizations under suspension conditions [9]. In such reactions, the enhancement of the initiation process is occurring *via* a mono-electronic transfer reaction between the peroxide and the iron(II) species, leading to the cleavage of the O-O bond into a radical and an anion together with the formation of the oxidized iron(III) derivative according to the well-known Haber-Weiss reaction (scheme 1) [10].



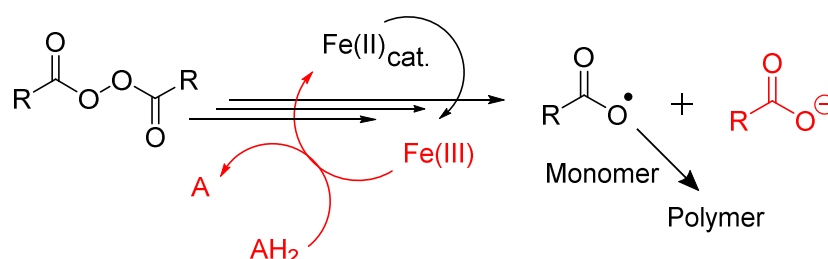
**Scheme 1.** Radical formation via redox peroxide decomposition using stoichiometric iron(II) as activator

Following the same principle, ferrocenyl compounds used in stoichiometric amounts *vs.* peroxide have been extensively described as excellent activators for peroxides decomposition, which has been applied in polymerization reactions under homogeneous conditions involving styrene and methyl methacrylate monomers [11-15]. However, the amount of iron in the overall polymerization process must be considered carefully for several reasons: *i*) iron derivatives are known to affect the quality of the polymer if present in high concentration, *e.g.* in an amount equal or close to that of the peroxide, which may facilitate the oxidation process during the lifetime of the polymer, thus contributing to reduce its thermal stability [16,17]; *ii*) iron can also accelerate the termination of radical polymerization when present in its higher oxidation state [18] and *iii*) iron can interfere with the presence of surfactant in emulsion or suspension polymerization, typically polyvinyl alcohol (PVA), which is necessary to stabilize the medium and obtain polymer particles with the required size and appropriate properties, for example through ionic-dipole interactions between iron and hydroxyl groups (-OH) in polymeric chains of PVA [19-21]. The surfactant properties of the latter would be weakened, leading to a disruption of the polymerization medium and damaging the physical properties of the final polymer.

For all these reasons, the use of metals in reduced quantities is a fundamental for the efficiency of the polymerization without compromising the progress of the process and interfering with the system components.

In this regard, the gradual addition of PAA in conjunction with small amounts of copper or iron water-soluble salts during the course of vinyl chloride polymerization, in bulk or in microemulsion, initiated *via* peroxyesters or diacyl peroxide decomposition, has been reported as a means to improve the polymerization in terms of berries formation [22]. This procedure is

very similar to that previously described in a patent regarding the polymerization of vinyl acetate in suspension using a dual-component ferrocene/water-soluble reducing agent for benzoyl peroxide decomposition (ferrocene, abbreviated as Fc, is biscyclopentadienyl iron  $\text{Cp}_2\text{Fe}$ ,  $\text{Cp} = \text{C}_5\text{H}_5$ ) [23]. Other examples in the literature deal with similar iron based dual-component redox initiators associated with a radical generator for the polymerization of vinyl monomers under biphasic conditions [24-26]. In all these cases, only catalytic amounts of the metal component are used, together with higher amounts of the reducing agent, whose role is assigned to regenerate the iron(II) species from its oxidized iron(III) form resulting from the redox reaction described in Scheme 1. Considering that the standard redox potentials of the reducing agent and of  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  in the iron component would be in adequation (for example 0.06 volt and 0.40 vs. ENH, for AA and Fc, respectively) [27,28], the behavior of this dual-component [metal catalyst/regenerator] activating system, referred to as a “kicker” [29], towards peroxide decomposition, can then be summarized as illustrated in Scheme 2, with the reducing agent being represented by  $\text{AH}_2$ .



**Scheme 2.** Peroxide decomposition using catalytic amounts of Fe(II) compound in the presence of a reducing, regenerative reagent  $\text{AH}_2$ .

Taking into account the mechanism depicted in Scheme 2, one could be confident towards its easy application to the radical polymerization of vinyl monomers, though there are several key barriers that need to be considered owing to the biphasic nature of the overall reaction, specifically in suspension. In particular, with organic peroxides, it would be judicious to involve a monomer-soluble iron compound like Fc, but the amphiphilic character of the ferrocenium cationic species associated with its counter-anion hampers an immediate regeneration of the iron(II) activating species inside the monomer droplets. Therefore, the nature and the amphiphilic properties of the  $\text{AH}_2$  reducing agent must also be tuned so that the overall regeneration process occurs more rapidly than the conventional thermo-initiated decomposition of the peroxide into two radicals.

The purpose of this paper is to present our findings on the kicker-activated polymerization of VAc and VCM, along with preliminary results on methyl methacrylate, under typical suspension conditions used in the industrial PVC synthesis, aiming at the improvement of the decomposition rate of peroxides using the above considerations. The peroxides have been chosen within those commonly used in industrial PVC synthesis, namely lauroyl peroxide (LPO) and di(2-ethylhexyl)peroxydicarbonate (EHP). Studies and analysis on the decomposition of EHP peroxide catalyzed by the kicker system (Fc as peroxide activator and  $\text{AH}_2$  as Fc regenerator) have first been performed in a medium that mimics that of suspension polymerization, focusing on monitoring the efficiency and the direct effect of the kicker through the evaluation of the peroxide decomposition kinetics. Subsequently, the decomposition of EHP in the presence of the kicker systems evaluated upstream has been thoroughly investigated, using a specific calorimeter reactor, under typical industrial suspension conditions of the

polymerization of VCM, which resulted in optimized conditions for the use of a kicker system to improve the efficiency of the initiation reaction and thus the synthesis process of PVC in suspension.

## Experimental

### *Materials and methods*

All operations (polymerizations and EHP decompositions) were conducted under dry argon or nitrogen by using Schlenk techniques. Ascorbic acid (AA), 6-O-palmitoyl-*L*-ascorbic acid (PAA), citric acid (CA), formic acid (FA), lactic acid (LA), 1-chlorobutane (*n*-BuCl), ferrocene (Fc), ferrocenium hexafluorophosphate ( $[\text{Fc}^+][\text{PF}_6^-]$ ) were commercial products and used without further purification. Vinylacetate (VAc) and ethyl acetate (Aldrich) were purified before use by distillation. Vinyl chloride monomer (VCM) is supplied in liquid form in equilibrium with its vapor pressure from Vynova Tessengerlo. Lauroyl peroxide (Laurox LPO-W40, LPO) and di-(2-ethylhexyl) peroxydicarbonate (Trigonox EHP-W60, EHP) used as pre-initiators were supplied by Akzo Nobel in the form of suspension (40 wt% in water) and emulsion (60 wt% in water/methanol), respectively. Primary polyvinyl alcohol (PVAI) was received from Nippon Gohsei (UK) Limited under the trade name GOHSENO<sup>TM</sup> K-type (in fact poly(vinyl alcohol-*co*-vinyl acetate that is manufactured as type 1 or type 2, with hydrolysis degree DH = 71-73.5 or 80%, respectively). Secondary polyvinyl alcohol (PVAII) was received from the same manufacturer under the trademark of WD100 (DH = 45%). They were used without further purification. Hydroxypropyl methylcellulose (HPMC) was received from the Dow Chemical Company Limited under the trade name Methocel F50. GC measurements were performed on a Varian 430, with FID detector heated to 250 °C and injected volume 1  $\mu\text{L}$  in split mode (dilution solvent isopropanol). SEC analysis was performed in THF as an eluent at 40 °C (1 mL/min) with a SIS HPLC pump (Waters S.A.S., France), a Waters 410 refractometer, and Waters Styragel columns (HR2, HR3, HR4, and HR5E) calibrated with polystyrene standards.  $M_n$  and  $M_w$  were determined against polystyrene standards and were corrected by using the Universal Calibration with the following Mark–Houwink parameters for PVAc:  $K = 1.56 \times 10^{-2} \text{ mL}\cdot\text{g}^{-1}$ ,  $a = 0.708$  [30]. Thermal properties of PVC were determined by the Polymer Technology Laboratory of Vynova-Tessengerlo in the form of a transparent soft film formulation, so-called CaZn, in which a PVC sample is mixed with a group of ingredients (plasticizers, stabilizers and lubricants), then processing the PVC/additives dry blend to a milled sheet on a two rolls mill, and heating for 5 minutes at 170 °C. The color measurements (melt color  $b^*$ , representing the short-term stability of PVC) on such samples were performed using a Minolta CM-2600d colorimeter.

VCM polymerizations were carried out in a micro-reactor Chemical Process Analyzer (CPA202 from ChemiSens (Lund, Sweden). CPA202 consists of a calorimeter reactor equipped with a stainless-steel stirrer and a glass jacket, with a bottom containing constant thermal zone consisting of hundreds of temperature sensors, and an advanced Peltier element which acts as a reversible heat pump to absorb or emit heat to (or from) the reactor. It holds up to 250 mL and works at a temperature between -50 and 200 °C, at a pressure up to 20 bar. Information from the reactor (temperature, pressure, energy, stirring current, pH...) is transferred in real-time and displayed directly on the computer, allowing for a very accurate follow-up of the

chemical process. This thermochemical analysis is carried out in two separate stages. The first one, during 30 minutes at the beginning of the reaction, is aimed at the evaluation of the energy required to reach the reaction temperature for standard s-PVC synthesis (*i.e.* 53 °C in the case of EHP peroxide). The second one is characteristic of the polymerization rate at this temperature where, after calibration, the amount of heat exchange required to stabilize the exothermic reaction at this temperature allows to follow the evolution of the conversion in time, by calculating the so-called Total Power (expressed in watts). The latter represents the calculated energy exchanged between the polymerization medium and the reactor, and it is calculated according to complex equations that are included in the reactor programming. When the polymerization medium is in a state of receiving heat, the Total Power value is negative, and vice versa when the polymerization medium is cooled, its value becomes positive. In addition, since VCM polymerization is exothermic, Total Power can be translated as VCM conversion. So, the integration of the Total Power at a time  $t$  over the whole of Total Power during the polymerization reaction gives the conversion of VCM at that time, taking into account the amount of VCM at  $t = 0$  and the final weight of PVC at the end of the polymerization.

*Peroxide decomposition procedure.* The decomposition of the EHP peroxide was carried out in a Schlenk tube under inert atmosphere conditions, eliminating all possible side reactions with oxygen, and in a typical suspension medium. The following recipe has been formulated to match the peroxide decomposition as in the industrial VCM polymerization medium: H<sub>2</sub>O (6.67 mL), *n*-BuCl solvent (3.75 mL, 50 wt%/H<sub>2</sub>O), suspending agents (PVAI) (3.3 mg, 0.1 wt%/n-BuCl), and pre-initiator (EHP) (9 mg,  $2.6 \times 10^{-5}$  mol) were charged in a Schlenk tube. Then, the suspension was degassed with argon. Deoxygenated Fc (1 mol%/EHP,  $v = 1$  mL, in solution in *n*-BuCl,  $C = 2.6 \times 10^{-4}$  M) and regenerator (50 mol%/EHP,  $v = 1$  mL, in solution in water) were injected, and the mixture was stirred and heated up to a given temperature. The conversion of peroxide during the reaction was determined by assaying the residual peroxide in the Schlenk tube at any desired time by iodometric titration.

*Iodometric titration.* After the peroxide decomposition at a given time, an aliquot was withdrawn, in which isopropanol was added to homogenize the suspension, then an excess of potassium iodide (KI) relative to the EHP peroxide, and acetic anhydride (3 mL). The mixture was stirred and heated at 80 °C for a few minutes. The iodine produced by the reaction between iodide and peroxide (yellow color) was titrated by sodium thiosulphate (0.005 M) until discoloration. All operations were performed under inert atmosphere (argon). The conversion of peroxide at a given time was calculated based on Equation 1.

$$\text{Conversion}(t) (\%) = 100 - \frac{V_e(t)}{V_e(t=0)} \times 100 \quad (\text{Eq. 1})$$

$V_e$ : spilled volume of sodium thiosulphate at equilibrium

*Coloration test on the ferrocenium (Fc<sup>+</sup>) reduction.* An homogeneous blue solution of [Fc<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] (2 mg, 6 μmol, in 1 mL water) was prepared, then a molar amount of 300 μmol of reducing agent was added. The appearance of a yellow color (typical of Fc) indicates that the reduction takes place.

### **Polymerizations procedures**

All polymerizations were performed using mixtures of the monomer and water under stable suspension conditions, obtained *via* the use of PVA or Methocel as dispersants.

*VAc polymerization.* In a typical experiment, a degassed Schlenk tube were introduced successively 2 mL of demineralized water, peroxide pre-initiator (0.1 mol% vs. VAc, *i.e.* 6.5 mg of pure LPO peroxide, 16.2 mg of suspension of Laurox LPO-W40, or 5.6 mg of pure EHP peroxide, 9.4 mg of emulsion of Trigonox EHP-W60, corresponding to 4660 or 4014 wt ppm/VAc of LPO and EHP, respectively), PVA I (0.7 mg, 500 wt ppm/VAc) and VAc monomer (1.395 g, 16.2 mmol). The reactor was then heated up to a given temperature. The kicker was added using a syringe *via* the septum on the top of the tube. The lipophilic components of kicker (typically Fc) are solubilized in ethanol (injection of 0.5 mL), and the hydrophilic ones (typically AA) are solubilized in water (injection of 0.5 mL). Samples were taken at different times and diluted in isopropanol in order to be analyzed by GC.

*VCM polymerization.* In a typical experiment, demineralized water (100 mL), the appropriate surfactant (1000 wt ppm/VCM, 50 mg) and peroxide pre-initiator (1456 or 1675 wt ppm/VCM, corresponding to 0.0728 g ( $2.1 \times 10^{-4}$  mol) of pure peroxide, 0.1213 g of emulsion of Trigonox EHP-W60 or 0.0835 g ( $2.1 \times 10^{-4}$  mol) of pure peroxide, 0.2094 g of Laurox LPO-W40 suspension, for EHP and LPO, respectively) were weighed and loaded into the reactor. Then, the reactor was closed, emptied of oxygen and purged with nitrogen. Thereafter, a weighed amount of VCM (50 g, 0.8 mol) was charged into the reactor. The mixture was then stirred at a speed of 950 rpm, and heated up to 53 °C. The warming lasted about 30 min with a rate of 1 °C/min. The temperature was kept constant during the reaction, and the time when the polymerization was considered to be started is when the temperature had reached 53 °C. The kicker was added before VCM loading or injected during the polymerization using a syringe *via* the septum on the top of the reactor. The lipophilic components of kicker (typically Fc) were solubilized in degassed ethanol (injection of 0.5 mL), and the hydrophilic ones (typically AA) are solubilized in degassed water (injection of 0.5 mL).

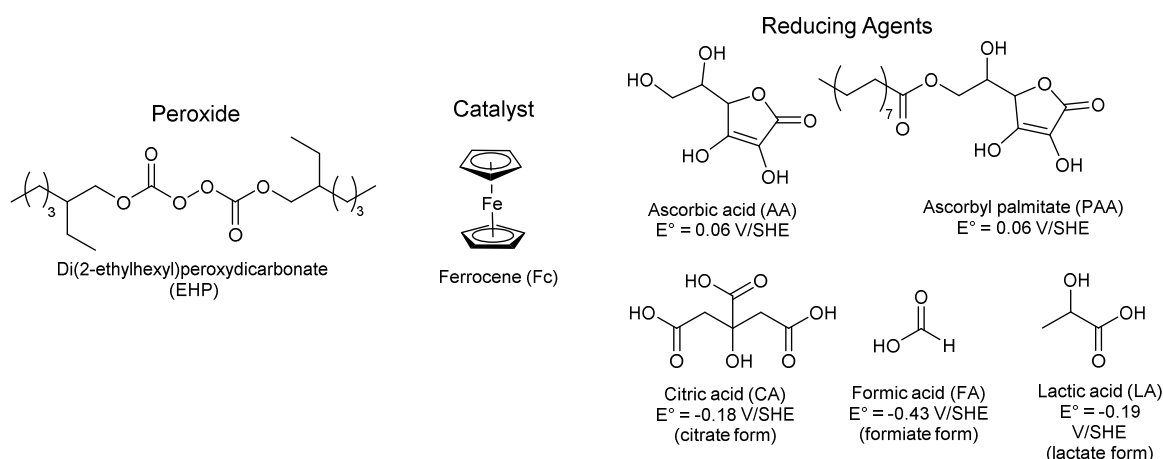
## Results and discussion

### Peroxide decomposition

The evaluation of the kinetic profile of the decomposition of EHP peroxide as a function of time at 53 °C and 40 °C, under suspension conditions (dispersion of *n*-BuCl in water, as a model of VCM phase) and in the presence of PVAI surfactant was undertaken. A set of reducers have been selected according to their redox potential value in order to be able to reduce  $\text{Fc}^+$  to Fc, including citric acid (CA), formic acid (FA), lactic acid (LA), ascorbic acid (AA) and ascorbic acid palmitate ester (or ascorbyl palmitate, PAA) (Chart 1).

The results are illustrated in Tables 1 and 2. The theoretical decomposition rate is determined on the basis of first-order Equation 2, with  $k_d$ , the decomposition constant of EHP peroxide, equal to  $45 \times 10^{-6} \text{ s}^{-1}$  at 53 °C based on AkzoNobel database [31], for a sample of EHP present at 60 wt% in water/methanol emulsion.

$$\text{Conversion}(t) (\%) = (1 - e^{-k_d t}) \times 100 \quad (\text{Eq. 2})$$



**Chart 1:** Dual-component kicker compounds studied for redox EHP decomposition

**Table 1.** Decomposition of EHP peroxide under suspension conditions at 53 °C

Run <sup>a</sup>	Kicker <sup>b</sup>	Conv 0.5 h <sup>c</sup> (%)	Conv 2 h <sup>c</sup> (%)	Conv 4 h <sup>c</sup> (%)
-	- <sup>d</sup> (theoretical)	7	27	46
<b>1.1</b>	- <sup>e</sup> (experimental)	8	24	44
<b>1.2</b>	Fc <sup>f</sup>	9 [1]	25 [1]	48 [4]
<b>1.3</b>	Fc/CA <sup>g</sup>	20 [12]	42 [18]	56 [12]
<b>1.4</b>	Fc/FA	18 [10]	40 [16]	60 [16]
<b>1.5</b>	Fc/LA	16 [8]	39 [15]	61 [17]
<b>1.6</b>	Fc/AA	44 [36]	63 [39]	80 [36]
<b>1.7</b>	Fc/PAA	43 [35]	64 [40]	75 [31]
<b>1.8</b>	CA <sup>h</sup>	8 [0]	20 [-]	35 [-]
<b>1.9</b>	FA <sup>h</sup>	10 [2]	23 [-]	38 [-]
<b>1.10</b>	LA <sup>h</sup>	6 [-]	17 [-]	35 [-]
<b>1.11</b>	AA <sup>h</sup>	20 [12]	40 [16]	70 [26]

<sup>a</sup> Results measured by the iodometric assay method, averaged over three measurements; <sup>b</sup> kicker 1/50 mol% vs. EHP; <sup>c</sup> in brackets: conversion gain by kicker by subtracting the contribution of experimental thermal decomposition; <sup>d</sup> calculation of the residual EHP peroxide based on Equation 2; <sup>e</sup> decomposition of EHP under suspension conditions as described above; <sup>f</sup> Fc alone (1 mol% vs. EHP); <sup>g</sup> NaHCO<sub>3</sub> was added to control the pH and forms citrate salt; <sup>h</sup> reducing agent alone (50 mol % vs. EHP).

According to Table 1, the thermal decomposition of peroxide under our suspension conditions (run 1.1) is quite consistent with the one corresponding to the theoretical decomposition (values given in the first row): the rate of the decomposition is following a 1<sup>st</sup>-order law with a decomposition constant equal to  $k_{d(\text{exp})} = 39 \times 10^{-6} \text{ s}^{-1}$ , which is close to the value found in the literature.<sup>24</sup> This gives credibility to the titration method that will be used later to follow the kinetics of decomposition. It should be noted that the present study is based on the decomposition of peroxide in the *n*-BuCl droplets suspended in water, whereas the theoretical decomposition is an account of EHP decomposition of a sample in a water/methanol emulsion. The addition of Fc (1 mol% vs. EHP, run 1.2) showed no activation, which clearly indicates that when Fc oxidizes to Fc<sup>+</sup>, it no longer participates in peroxide decomposition under these suspension conditions that arises mainly from the thermal contribution. This result is similar to



what was found in the literature using, for example, ethyl methyl ketone peroxide but in contrast to dibenzoyl peroxide, where a small amount of Fc (*ca.* 2 mol% relative to the peroxide) can accelerate the decomposition. In this case, the ferrocenium-benzoate complex is dissociated into Fc and benzoate radical, allowing the Fc to pursue the decomposition reaction [32]. Therefore, a means of regenerating Fc becomes necessary in our case. For instance, the introduction of the dual-component kicker system (runs 1.3-1.7) led to a significant acceleration of EHP decomposition, bearing in mind that Fc is introduced in catalytic amount (1 mol% *vs.* EHP). This means that for the majority of the runs, the reductant (AH<sub>2</sub>) has regenerated the Fc and activated the catalytic cycle of peroxide decomposition as already described above. Among these regenerators, AA and PAA, both associated with Fc, seem to be the most efficient ones at activating the decomposition, allowing the reaction rate to be enhanced by a factor of 5 in the early stages (up to 30 min) of the reaction. After that time, the acceleration rate of decomposition by the kicker started to decrease, by a factor of 2.7 and 1.85 after 2 h and 4 h, respectively (runs 1.6 and 1.7).

In fact, the decomposition of the peroxide takes place owing to two effects operating in parallel, thermal decomposition and redox decomposition by the kicker. By subtracting the thermal decomposition contribution (run 1.1) we observed that at *t* = 0.5 h, the Fc/AA kicker (run 1.6) decomposed *ca.* 36 % of EHP, then an additional 3 % (39 %) after 1.5 h and nothing more (36 %) after that time. The same is observed for the other regenerators, where for example Fc/CA kicker (run 1.3) decomposed 12 % of EHP during the first 0.5 h, then 6 % more after 1.5 h, and nothing after. Finally, the reducing agents alone did not display much impact on the decomposition of EHP (runs 1.8-1.10), with the exception of AA. We noticed that AA alone can decompose the peroxide but more slowly than when combined with Fc within the kicker, except for long reaction times (run 1.11 *vs.* run 1.7).

**Table 2.** Decomposition of EHP peroxide under suspension conditions at 40 °C

Run <sup>a</sup>	Kicker <sup>b</sup>	Conv 0.5 h <sup>c</sup> (%)	Conv 2 h <sup>c</sup> (%)	Conv 4 h <sup>c</sup> (%)
-	- <sup>d</sup> (theoretical)	1	3	5
<b>2.1</b>	- <sup>e</sup> (experimental)	2	4	6
<b>2.2</b>	Fc/CA	12 [10]	19 [15]	26 [20]
<b>2.3</b>	Fc/AA	30 [28]	45 [41]	65 [59]

<sup>a</sup> Results measured by the iodometric assay method, averaged over three measurements; <sup>b</sup> kicker 1/50 mol% *vs.* EHP; <sup>c</sup> in brackets: conversion obtained by subtracting the contribution of experimental thermal decomposition; <sup>d</sup> residual peroxide calculation of EHP based on Equation 2; <sup>e</sup> decomposition of EHP under suspension conditions as described above.

With respect to the data presented in Table 2 for the decomposition of EHP peroxide at 40 °C, the results clearly show that Fc/AA (run 2.3) decomposed about 30% of EHP after 0.5 h, then 45 % after 2 h (+15 % within 1.5 h) and 65 % after 4 h of reaction (+ 20 % within 2 h). At this temperature, the redox decomposition of EHP by Fc/AA was much more effective than the thermal decomposition, which appeared to be negligible (run 2.1). However, this kicker activity gradually decreased with time. The effect of the kicker involving CA as reducing agent is clearly lower (run 2.2) when compared to the Fc/AA couple.

In general, the strong activation caused by Fc/AA or Fc/PAA compared to other kickers could be related to two factors: *i*) the immediate regeneration of Fc<sup>+</sup> by AA in the mixture, as we confirmed by a coloring test: the blue color of Fc<sup>+</sup> immediately turns into a yellow color of Fc after the addition of AA; *ii*) the fact that AA, in contrast to other reducing agents evaluated, can

interact itself and directly reduce EHP peroxide without the addition of Fc, as shown in Table 1 (run 1.11 vs. runs 1.8-1.10), and in accordance with what has been previously mentioned in the literature [33].

### Vinyl acetate (VAc) polymerization

The polymerization of VAc (1000 eq vs. peroxide) was performed under suspension conditions at 53 °C using the procedure as described above (see experimental), in the presence of selected ratios of Fc/AA redox combinations and PVAI surfactant, with the aim to compare them with each other regarding their effect towards the activation of EHP and LPO peroxides. The results are reported in Table 3.

**Table 3.** Suspension polymerization of VAc using EHP or LPO in the presence of Fc/AA

Run <sup>a</sup>	Fc/PO/AA <sup>b</sup>	Conv. (%)				
		5 min	10 min	20 min	30 min	60 min
3.1	0/1/0	6	12	24	-	-
3.2	0.5/1/0	-	19	19	-	-
3.3	0.4/1/0	-	19	20	-	-
3.4	0.3/1/0	-	20	22	-	-
3.5	0.2/1/0	-	20	24	-	-
3.6	0.1/1/0	-	17	23	-	-
3.7	0.05/1/0	-	17	23	-	-
3.8	0/1/0.5	-	14	27	-	-
3.9	0/1/0.5 <sup>c</sup>	-	13	25	-	-
3.10	0.2/1/0.5	35	39	39	-	-
3.11	0.1/1/0.5	34	45	49	-	-
3.12	0.05/1/0.5	28	45	59	-	-
3.13	0.01/1/0.5	19	32	54	-	-
3.14	0.01/1/0.25	16	35	60	-	-
3.15	0.01/1/0.5 <sup>d</sup>	8	17	32	-	-
3.16	0/1/0	-	-	-	10	20
3.17	2/1/0	-	-	-	30	30
3.18	1/1/0	-	-	-	35	41
3.19	0.5/1/0	-	-	-	37	46
3.20	0.3/1/0	-	-	-	28	39
3.21	0.2/1/0	-	-	-	24	35
3.22	0.1/1/0	-	-	-	18	26
3.23	0/1/0.5	-	-	-	14	25
3.24	0/1/0.5 <sup>c</sup>	-	-	-	7	12
3.25	0.5/1/0.5	-	-	-	90	95
3.26	0.5/1/0.5 <sup>c</sup>	-	-	-	57	92
3.27	0.2/1/0.5	-	-	-	64	95
3.28	0.1/1/0.5	-	-	-	52	94

<sup>a</sup> Reactions conducted at 53 °C in suspension with PVAI, VAc/PO (peroxide) = 1000/1; <sup>b</sup> PO = EHP (runs 3.1 – 3.15) or LPO (runs 3.16 – 3.28), <sup>c</sup> PAA was used instead of AA; <sup>d</sup> Fc\* was used instead of Fc.

Entries 3.1-3.15 are related to the use of EHP, commonly employed in such suspension radical polymerization reactions. One can observe that the addition of Fc in the medium from 0.5 eq to 0.05 eq vs. peroxide substantially enhances the conversion at 10 min, *i.e.* the initial

polymerization rate (runs 3.2-3.7) *vs.* run 3.1 in absence of Fc, as expected from results already reported on the activation of peroxides for methyl methacrylate and styrene polymerization [11-15]. However, this initial burst is lost after a short period of time: after 20 min, all tests become less productive than the polymerization initiated by thermal activation of peroxide. One can propose that the increase in the reaction rate is probably correlated to the decomposition of EHP as shown in Scheme 2, which leads to the rapid formation of a radical and the corresponding anion of EHP, along with the ferrocenium species that migrates in the aqueous phase. Indeed, it turns out that the color of the reaction medium in these reactions rapidly changes from yellow to green then blue within a few minutes. Thereafter, the iron derivative in its oxidized form remains in the aqueous phase where it can no longer interact with EHP. Using AA or its ester derivative PAA without Fc has no overall effect over the peroxide decomposition and thus on the polymerization (runs 3.8, 3.9). In contrast, polymerizations using EHP and Fc conducted in the presence of AA in excess *vs.* Fc (runs 3.10-3.13) showed no such color change with time. However, even if the experiment using 0.2 eq of Fc and 0.5 eq of AA gives the highest initial reaction rate (multiplied by a factor of *ca.* 6 *vs.* EHP alone, runs 3.10 *vs.* 3.1, respectively), no further polymerization was observed for  $t > 5$  min, likely due to an excessive peroxide decomposition. Accordingly, this drawback is easily solved upon reducing the Fc (runs 3.10-3.13) or AA (runs 3.13, 3.14) contents, where using amounts as low as 1 mol% Fc associated with 25 mol% AA *vs.* EHP is found to be the best compromise. An enhancement of the polymerization rate of a factor of *ca.* 2 to 3 is then observed, while maintaining the peroxide content at such a level that the reaction can go to completion. In addition to this study, it should be noted that replacing Fc with its permethylated counterpart Fc\* results in a much lower efficiency in terms of EHP decomposition and consequently a lower conversion of VAc to PVAc under the experimental conditions used (run 3.15).

Runs 3.16-3.28 are representative of the reaction conducted with LPO as peroxide. Due to a longer half-life of this peroxide (28.3 h *vs.* 4.3 h for EHP at 53 °C) [31], the reactions were monitored over longer reaction times. Under thermal activation alone (run 3.1), the reaction course follows an apparent zero order, the conversion being directly proportional to the reaction time until completion. A different behavior is observed upon introduction of Fc from the beginning of the reaction: introducing this compound alone from 2 eq to 0.1 eq *vs.* peroxide (runs 3.17-3.22) induced a substantial enhancement of the initial reaction rate, in a similar manner to that observed above with EHP. However, upon analysis of the conversion after 0.5 h, it obviously appears that the use of Fc in excess (runs 3.17-3.19) is detrimental to the evolution of the reaction, owing probably to a too extensive consumption of the peroxide, according to Scheme 1, during the first 30 min period. This is particularly relevant in run 3.17, where a maximum of 30% conversion is noted after 0.5 h, without any further polymerization [34]. Using AA without Fc has only rather small effect on the reaction course, in line with little contribution to the peroxide decomposition (run 3.23), while its ester derivative PAA acts as partial inhibitor (run 3.24). In contrast, significant improvements in monomer conversion occurred when using dual-component activating systems consisting of mixtures of ascorbic acid (AA) or palmitate ester (PAA) associated with Fc (runs 3.25-3.28). Using 50 mol% of both activators in equimolar amounts of Fc and AA allowed the reaction rate to be enhanced by a factor of 9, giving rise to a 90% conversion after 0.5 h. Although less reactive, the use of lower

amounts of Fc gives interesting activation rates, in particular when using 0.1 eq of Fc *vs.* peroxide (run 3.28).

It appears then that combining Fc and AA as further reductant is a key factor for controlling the polymerization rate in a way by which the reaction is occurring until completion. Rather relevant in this context is the comparison between runs 3.19 and 3.25, which shows that regeneration of Fc by AA from ferrocenium  $\text{Fc}^+$  allows for stabilizing the amount of Fc species responsible for the production of the radical initiator. Interestingly, with LPO, the palmitate derivative PAA seems to operate more gradually as the kicker co-component than its more hydrophilic counterpart AA towards the overall polymerization time (runs 3.26 *vs.* 3.25). It must finally also be pointed out at this stage the usefulness of ferrocenium reduction to avoid large amounts of this cationic species in the reaction medium. Indeed, in separate experiments, using stoichiometric amounts of ferrocenium salts *vs.* LPO during polymerization of VAc completely inhibited the reaction: a dual role of AA (or PAA) can therefore be assigned in this process, as it allows not only to regenerate the Fc activator, but also avoids at the same time the inhibitor effect of its oxidized form.

As stated in the introduction, peroxide decomposition using Fc has been thoroughly studied by some Russian groups, and several publications were devoted to the use of substituted ferrocene complexes for activating benzoyl peroxide in methyl methacrylate polymerization under homogeneous conditions [35]. Accordingly, we decided to assess a series of commercially available substituted ferrocene complexes as potential kicker catalysts under our experimental conditions towards the polymerization of VAc. This comparison was made using EHP as peroxide (0.1 mol% *vs.* VAc monomer) with ferrocenyl complex/AA at 1/25 mol% or 2.5/50 mol% *vs.* EHP. The results are given in Table 4, where are reported the initial polymerization rates calculated from the slope of the curves (VAc conversion) *vs.* (time) at  $t = 20$  min (see Fig. S1 in the SI section).

**Table 4.** Reactivity comparison of different ferrocenyl iron complexes  $\text{Fe}(\text{Cp})(\text{Cp}^{\text{R}})$  towards EHP decomposition in VAc suspension polymerization in the presence of AA as reducing agent ( $\text{Cp}^{\text{R}}$  is for a substituted Cp ring).<sup>a</sup>

$\text{Fe}(\text{Cp})(\text{Cp}^{\text{R}})^{\text{a,b}}$	- (run 3.8 <sup>d</sup> )	Fc (run 3.13 <sup>d</sup> )	Fc* (run 3.15 <sup>d</sup> )	$\text{FeCp}(\text{Cp}^{\text{N}})^{\text{c}}$	$\text{FeCp}(\text{Cp}^{\text{CHO}})^{\text{c}}$	$\text{FeCp}(\text{Cp}^{\text{Ac}})^{\text{c}}$
Conv. 20 min (%)	27	54 (65 <sup>c</sup> )	32	39	28	29

<sup>a</sup> Suspension polymerizations conducted at 53 °C using VAc/ $\text{Fe}(\text{Cp})(\text{Cp}^{\text{R}})$ /EHP/AA (1000/0.01/1/0.25) molar ratio; <sup>b</sup>  $\text{Cp}^{\text{N}} = \text{C}_5\text{H}_4\text{CH}_2\text{NMe}_2$ ,  $\text{Cp}^{\text{CHO}} = \text{C}_5\text{H}_4\text{C}(\text{O})\text{H}$ ,  $\text{Cp}^{\text{Ac}} = \text{C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3$ ; <sup>c</sup> VAc/ $\text{Fe}(\text{Cp})(\text{Cp}^{\text{R}})$ /EHP/AA (1000/0.025/1/0.5) molar ratio; <sup>d</sup> see Table 3.

All these ferrocenyl-based complexes are found to activate the polymerization when compared to the experiment with AA alone (run 3.8). The conversions values indicated that the parent Fc, whatever the kicker amount, is the most efficient, as observed on the corresponding effect using benzoyl peroxide in MMA polymerization [35]. Following in terms of effectiveness are the N,N-dimethyl-N-(methylferrocenyl)amine substituted congener ( $\text{FeCp}(\text{Cp}^{\text{N}})$ ) and decamethylferrocene (Fc\*), whereas electron withdrawing substituents such as formyl (in  $\text{Cp}^{\text{CHO}}$ ) and acetoxy (in  $\text{Cp}^{\text{Ac}}$ ) groups are less suitable, playing a negligible role as kicker catalyst. Although this is still under debate, the mechanism of radical formation *via* this activation can be assumed to be similar to that suggested for benzoyl peroxide decomposition, where variations in the Fc structure result in a change of the transition state in the charge transfer

complex formation between the iron complex and EHP during the decomposition process [35]. However, under the present suspension conditions, other crucial parameters are the solubilities, mass transfer and/or partition coefficients of the ferrocenium species and AA between water and organic phase: both should be in a same phase to react, and these are certainly key points to be considered for the regeneration process to occur readily. This point will be emphasized later when applying the concept for vinyl chloride polymerization.

Beyond this activation procedure, one might wonder whether the resulting polymer could have different properties from those obtained using the non-activated standard radical process. Steric Exclusion Chromatography (SEC) analysis of a selection of polymers have been therefore compared with those coming from the classical thermal activated polymerization reaction (Table 5 and Fig. S2 in SI section). Examination of the results reveals that when using a low amount of Fc that leads to near complete conversions of VAc, the polymer characteristics are very similar: medium molar masses polymers are produced, with rather low dispersity considering a radical mediated polymerization, although a shoulder on the SEC curves indicates a somewhat bimodal distribution. Little deviations on the  $M_n$  values are observed when the reactions were not going to completion (runs 5.2 and 5.3), in which cases although the average  $M_n$  slightly increases compared to the reference without kicker (run. 5.1). This can be ascribed to the presence of high amount of Fc (10 and 5% in runs 5.2 and 5.3, respectively) and considering that kicker decomposition affords one radical per EHP (cf. Scheme 2) whereas thermal decomposition generates two radicals per EHP, albeit at a much slower rate. Furthermore, one can qualitatively observe on the chromatograms that the molar masses of the higher fractions are about twice as much as those of the lower fractions. This situation is not unusual in VAc polymerization as it is found during cobalt-mediated radical polymerization using LPO as initiator in bulk [36] as well as in suspension [37]; termination reactions by combination induced by particle coagulation and chain transfer to polymer are suggested to be responsible for this phenomenon. The higher content of the lower molecular weight fraction in runs 5.2 and 5.3 may be ascribed to a too rapid decomposition reaction of EHP, leading to an increase in temperature that favors the transfer to monomer ( $E_a = 41.6$  kJ/mol) vs. the transfer to polymer reaction ( $E_a = 37.7$  kJ/mol) [38].

**Table 5.** Influence of the Fc/AA kicker activation procedure on the PVAc polymers characteristics.

Run <sup>a</sup>	Fc/EHP/AA	Conv. <sup>b</sup>	$M_{n,SEC}$ <sup>c</sup>	$M_w/M_n$ <sup>c</sup>
5.1	0/1/0	92 %	38 700	2.17
5.2	0.1/1/0.5	47 % <sup>d</sup>	47 700	1.86
5.3	0.05/1/0.5	62 % <sup>d</sup>	47 200	1.89
5.4	0.025/1/0.5	86 %	39 200	2.07
5.5	0.01/1/0.5	93 %	34 900	2.28
5.6	0.005/1/0.5	93 %	35 800	2.24

<sup>a</sup> Using the same experimental conditions as in Table 4; <sup>b</sup> Final VAc conversion after 3 h; <sup>c</sup> determined by size exclusion chromatography (SEC, PS calibration) and after Mark-Houwink corrections for PVAc (see experimental section); <sup>d</sup> maximum VAc conversion after 1 h.

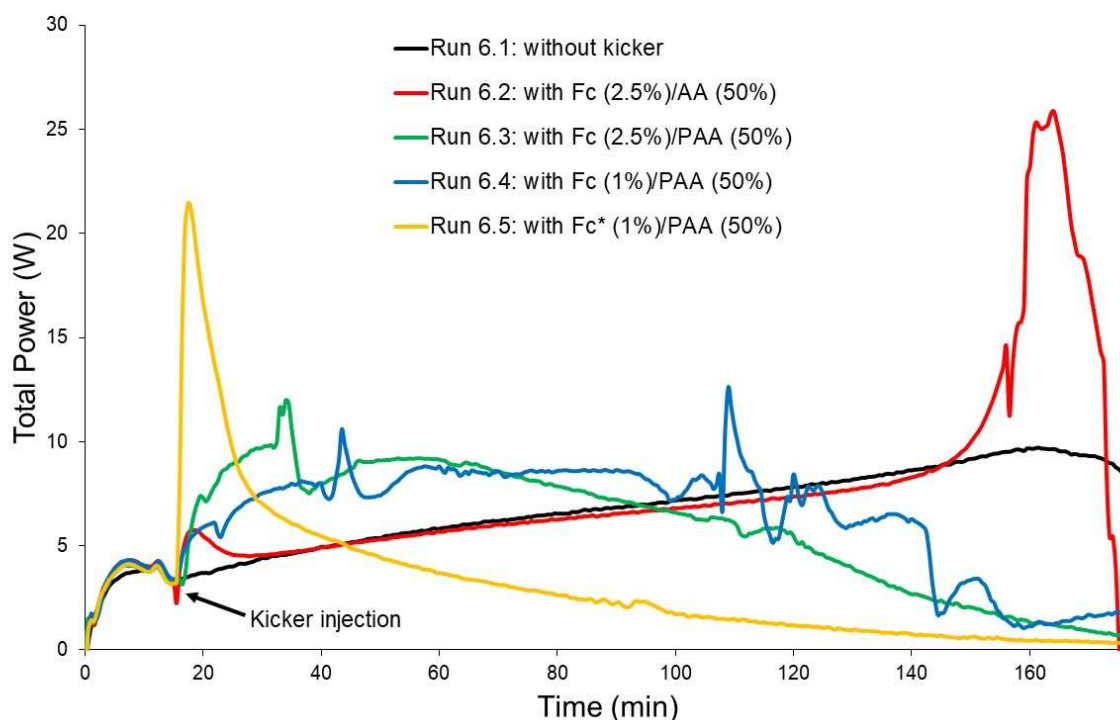
Following these results, the use of a similar activation procedure has been preliminarily attempted for the suspension polymerization of methyl methacrylate (MMA) under the same experimental conditions, using EHP as peroxide (see SI, Table S1). In contrast to what was

found with VAc monomer, the use of 0.2 eq of Fc alone as activator led to a strong enhancement of the reaction rate (run S1.2, Table S1), after some induction period in this suspension medium, which even persisted after 2 h. This is in line with previous results on the use of the Fc/benzoyl peroxide for MMA polymerization, where the ferrocenium-benzoyl salt itself is suggested to reversibly generate the benzoyl radical for further polymerization initiation [32] or possibly mediates the formation of a [ferrocenium-(PMMA)] growing species initially formed from the radical cation [39]. Interestingly, in our case, the addition of AA was beneficial in terms of controlling the polymerization rate throughout the reaction (run S1.3, Table S1), even with an amount of Fc as low as 1 mol% vs. EHP (run S1.4, Table S1).

### **Vinyl chloride polymerization**

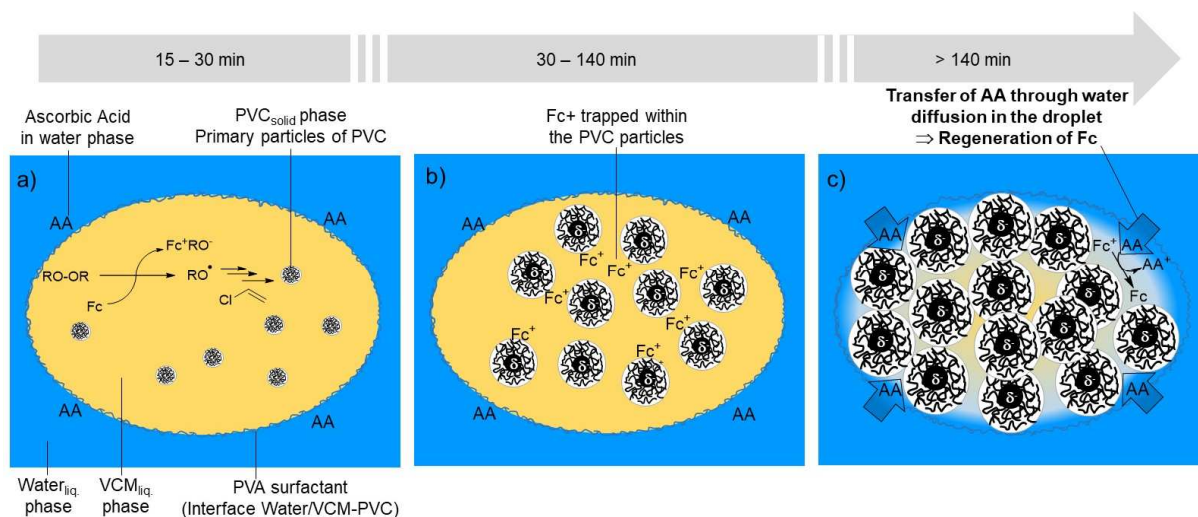
One major objective of this work was to provide an activator system for the synthesis of suspension PVC (s-PVC) from VCM polymerization. Due to the gaseous nature of the monomer, the reactions were conducted safely in a 250 mL glass reactor (CPA202 thermo-calorimeter, maximum pressure 20 bar), which allows monitoring all along the polymerization and until completion of the reaction progress. This equipment also enables to control the energy needed to reach the required reaction temperature that depends on the peroxide involved, as well as the energy required to cool this adiabatic device to stabilize the process at a given temperature (more details are given in the experimental section).

First experiments have been performed using EHP as a peroxide. The kinetic profile of a standard, non-activated reaction is given in Figure 1 (run 6.1, black line), where it is shown that the Total Power increases regularly until *ca.* 160 min. Then a decrease in the heat flow can be observed near the end of the monomer consumption, where the liquid/vapor equilibrium of the VCM monomer ceases to occur. This 160 min time corresponds to a *ca* 70% conversion of the monomer, which is the so-called critical conversion  $X_f$ . The next experiments were performed using the same procedure, but introducing the redox dual-component systems 15 min after attaining the thermally stabilized steady stage at 53 °C. Different mixtures of potential kickers have been assessed and their effect on the reaction course was compared with the classical, thermally initiated process (run 6.1 vs. runs 6.2-6.5, Fig. 1).



**Fig. 1.** Heat-flow curves comparison of VCM polymerizations conducted at 53 °C (black line: pure thermally activated; other colors: dual component activated systems); VCM/EHP = 3840/1(molar ratio); surfactant = PVAI (1000 wt ppm vs. VCM).

Run 6.2 has been first conducted for VCM polymerization using the Fc/AA dual-component system (2.5/50 mol% vs. EHP) (red line, Fig. 1) that was previously optimized for VAc (see the dedicated section, *vide supra*). An immediate but short living effect of Fc, of little intensity, was noticed just after introducing the activating system, after which the thermal/reaction profile was found to follow that of the non-catalyzed reaction. In contrast, a huge activation was observed by the end of the reaction (from *ca.*  $t = 140$  min), which could be related to a modification of the equilibrium exchanges between the free liquid monomer, polymer and gas phases, allowing a rapid and non-controlled decomposition of the peroxide. Obviously, this behavior is the result of the absence of regeneration of Fc from ferrocenium  $\text{Fc}^+$  during the main part of the process, which can be ascribed to the fact that AA and the  $\text{Fc}^+$  cation were located in different phases when VCM is in equilibrium between the liquid, vapor and PVC phases until the onset of the strong activation at *ca.* 140 min. Deviation from this situation appeared from the critical  $X_f$  point value (at *ca.* 70% conversion at 53 °C), when the free monomer liquid has been totally consumed [40]. Consequently, the monomer of the gas phase begins to diffuse towards the polymer phase, and water begins to penetrate PVC particles. As consequences, many chemical and physical factors of the polymerization medium are modified. This drastically changes the partition of the monomer, the peroxide, AA and  $\text{Fc}^+$  species within the polymer and water phases, leading to a rapid Fc regeneration process at this stage. This results in a tremendous acceleration of the reaction rate due to an uncontrolled decomposition of the peroxide. A possible explanation would be that, since PVC particles are considered negatively charged, an interaction can occur with the early generated  $\text{Fc}^+$ , which remains trapped within these particles [41]. This phenomenon fades as the conversion increases and, when the free liquid monomer is sufficiently consumed, water begins to penetrate the PVC particles, allowing AA to contact  $\text{Fc}^+$  at the PVC/water interface resulting in an abrupt activation (see Fig. 2).



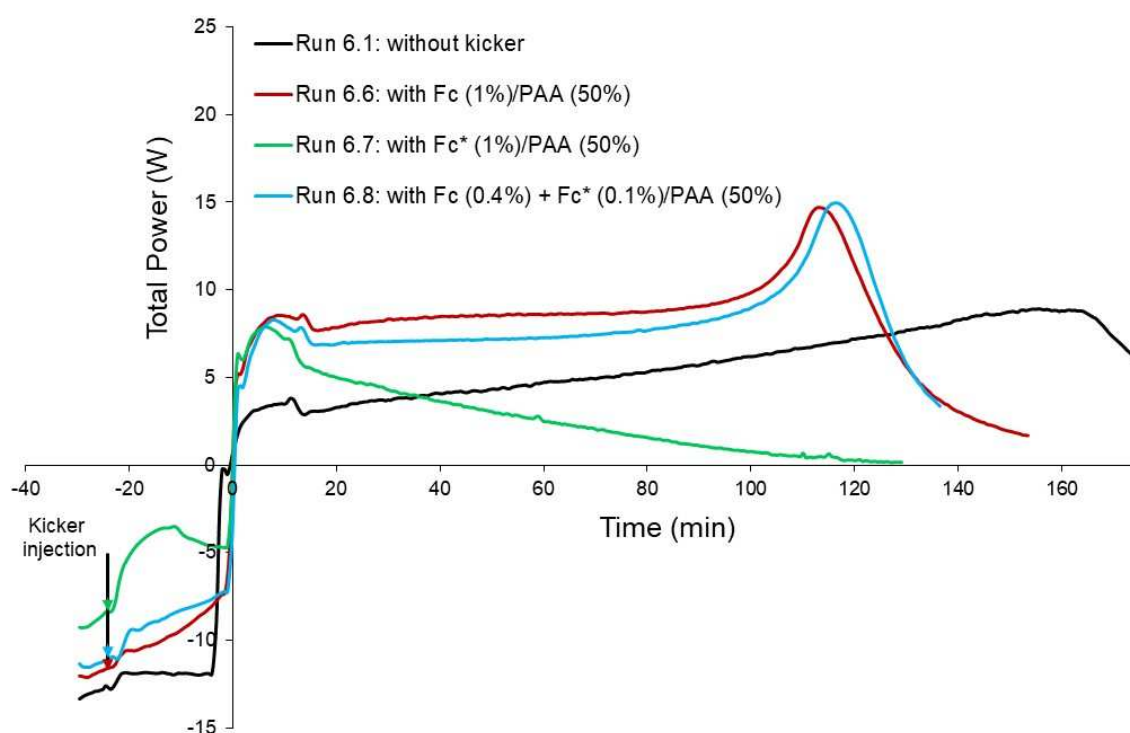
**Fig. 2.** Evolution of the reaction medium as a function of time; a) formation of primary PVC particles within the droplet of VCM resulting from the initiation of polymerization by thermal and redox decomposition of the peroxide (from  $t = 15$  to 30 min); b) formation of a continuous network of PVC particles within the droplet resulting only from the thermal decomposition of the peroxide, due to the trapping of  $Fc^+$  by the negatively charged particles (from  $t = 30$  to 140 min); c) After the consumption of a large amount of monomer, water enters the droplet while carrying AA, which results in the regeneration of Fc and leads to an abrupt decomposition of the peroxide ( $t > 140$  min).

To avoid this drawback of sudden and late exothermic activation, we anticipated that the use of a more lipophilic reducing agent might be a suitable alternative, as this would probably help the partition of this component in the same phase as the ferrocenium species. Pleasingly, using PAA, the palmitate ester of ascorbic acid (Chart 1), under the same conditions as before for AA (2.5% Fc, 50% PAA, run 6.3, green line, Fig. 1) at 53 °C revealed this hypothesis to be true. However, it led to a strong increase in temperature, likely due to a too rapid decomposition of all EHP, resulting in an upper limit of 65% conversion after 180 min. Reducing the amount of the Fc catalyst was then mandatory to allow for a slower and better controlled decomposition of EHP: the introduction of Fc/PAA (1:50 mol% vs. EHP) activating system after 15 min (run 6.4, blue line, Fig. 1) allowed the reaction to be completed within 140 min, when compared to 180 min without activator. Replacing Fc by decamethylferrocene ( $Fc^*$ ), with 1 mol%/EHP associated to 50% of PAA, the polymerization rate increased significantly immediately after its injection (run 6.5, yellow-orange line, Fig. 1). This could be due not only to the high reduction potential of  $Fc^*$  towards peroxide compared to Fc, but also likely to its greater solubility in the organic phase, allowing its oxidized form ( $Fc^{*+}$ ) to meet smoothly with PAA. However, this activity lasted only a short time (*ca.* 10 min), likely due to the complete decomposition of EHP peroxide without releasing enough radicals to polymerize the total amount of monomer. It can be argued that radicals are rapidly produced with  $Fc^*$  but not all of them would succeed in initiating the polymerization of VCM due to, among others, the occurrence of side reactions of  $Fc^*$  with radicals as it has been found for  $Fe^{2+}$  and  $H_2O_2$  peroxide under aqueous conditions [42].

Although these catalytic conditions were effective in terms of reactivity, comparison of their corresponding Total Power profiles with that in the absence of activator (Run 6.1, black line, Fig. 1) proved detrimental in controlling the temperature of the reaction mixture. As a matter of facts, the introduction of the lipophilic reducing agent PAA into a separate polymerization



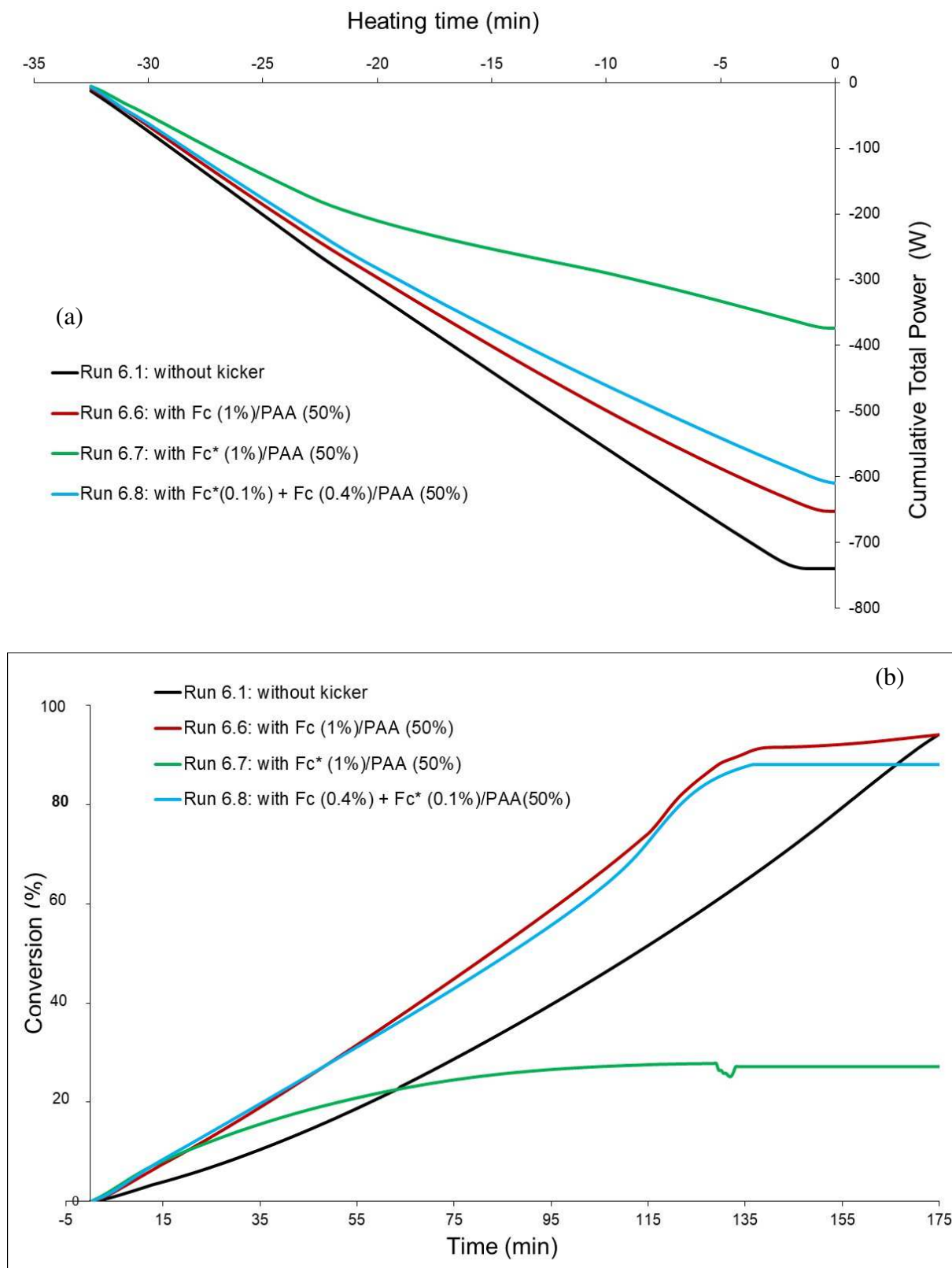
experiment using EHP in the absence of Fc induced a phase disruption within the suspension, which led to the crusting of the reaction mixture, making it unusable for any potential implementation of the process under industrial conditions. This experiment highlights that PAA also played a second role as a surfactant, in competition with PVAs, which was detrimental to the overall stability of the suspension mixture. Moving from PVAs to cellulosics as dispersing agents could solve this drawback, so that a further optimization of the catalytic process has been done using hypromellose (Methocel®) as surfactant. Experiments were performed under conditions where the activating system was introduced just after the loading of the overall [water/surfactant/VCM] mixtures in the reactor before heating. Two heat-flow diagrams using this procedure are presented in Figure 3 from the beginning of the reactions (stated at -30 min, preheating to 53 °C) to completion [43]. Following the previous promising results using PAA as kicker co-component with PVA surfactants, a first experiment has been conducted using Methocel® surfactant associated with Fc at a Fc/PAA molar ratio of 1/50 vs. EHP (run 6.6, red line, Fig. 3). Along with a much better control over the temperature during most of the polymerization, an interesting feature is observed during the preheating process, which consists of a strong reduction in the energy required for the reaction vessel to attain the desired temperature of 53 °C. The use of Fc at levels as low as 1 mol% vs. EHP associated with PAA under these conditions is then found to give an enhancement of the overall reaction rate, allowing the polymerization to be completed within *ca.* 2 h vs. 3 h under the reference conditions.



**Fig. 3.** Heat-flow curves comparison of VCM polymerizations (VCM/EHP = 3810/1, molar ratio) conducted at 53 °C using the Fc/PAA (run 6.6, red line), Fc\*/PAA (run 6.7, green line) and (Fc+Fc\*)/PAA (run 6.8, blue line) kicker system in the presence of Methocel® surfactant (1000 wt ppm vs. VCM). The kicker injection is performed directly after VCM loading.

By consideration of the polymerization experiment with Fc\*/PAA system (1/50 mol% vs. EHP) (run 6.7, green line, Fig. 3), where the introduction is performed directly after VCM loading into the reactor with Methocel® surfactant instead of PVAI, the polymerization rate tended to rise even before the required temperature was reached (between - 30 and 0 min). But as mentioned above, this efficiency did not last long (< + 20 min) and the rate started to decrease until it reached almost zero. By combining Fc\* (0.1 mol%) and Fc (0.4 mol%) along with PAA (50 mol%), a trace (run 6.8) very similar to run 6.6 was obtained but with half the amount of Fe.

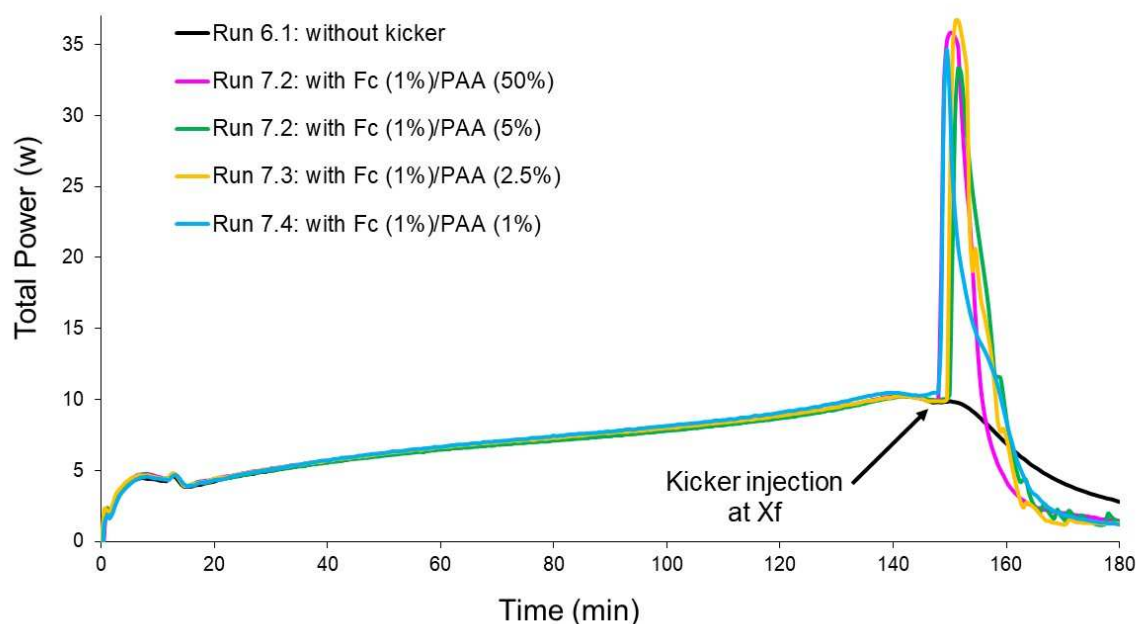
The energy consumption during the 30 min pre-heating time is presented in Fig. 4a, where the cumulative Total Power represents the total energy received by the reaction medium at a given time, which is the sum of the Total Power supplied from the start of heating (the negative time is the heating time where the reaction medium receives heat until  $t = 0$  min), until the temperature has reached 53 °C. From Fig. 4a, it appears that the use of the ferrocenyl-based activators with PAA reduces the energy required to reach a temperature of 53 °C: it clearly benefits from the exothermal decomposition reaction of EHP together with that of a polymerization process starting before rising the temperature to 53 °C. By using the more lipophilic Fc\* activator, a much more efficient decomposition reaction of EHP occurs, as indicated by a drastic reduction in the energy required to reach the reaction temperature, giving an energy saving of *ca.* 50% (green line, Fig. 4a). However, as a result, the reaction then failed to proceed to completion due a too fast decomposition of the peroxide. Reduction of the iron content *via* the use of a combination of Fc (0.4 mol% vs. EHP) and Fc\* (0.1 mol% vs. EHP) (light blue line, Fig. 4a) gave an energy savings of *ca.* 20% during the initial rise in temperature of this batch reaction, together with a kinetic profile close to the one found with 1 mol% Fc. Regarding the monomer conversion over the whole process, the Fc/PAA (1/50 mol% vs. EHP) kicker is found to be the most efficient system for accelerating the polymerization (red line, Fig. 4b). Also, although Fc\*/PAA is very effective in the pre-heating phase, it fails to lead to a total consumption of VCM, which is a very significant drawback (green line, Fig. 4b): the kicker effect decreases after *ca.*  $t = 20$  min where the conversion reaches a limit of 20 %. Switching to the combination of Fc and Fc\* resulted in no progress in this area (light blue line, Fig. 4b).



**Fig. 4.** Heat-flow time curve during preheating (a) and conversion vs. time of VCM polymerization (b) as a function of the activating system using EHP as peroxide. VCM/EHP = 3810/1 (molar ratio), Methocel® 1000 wt ppm vs. VCM.

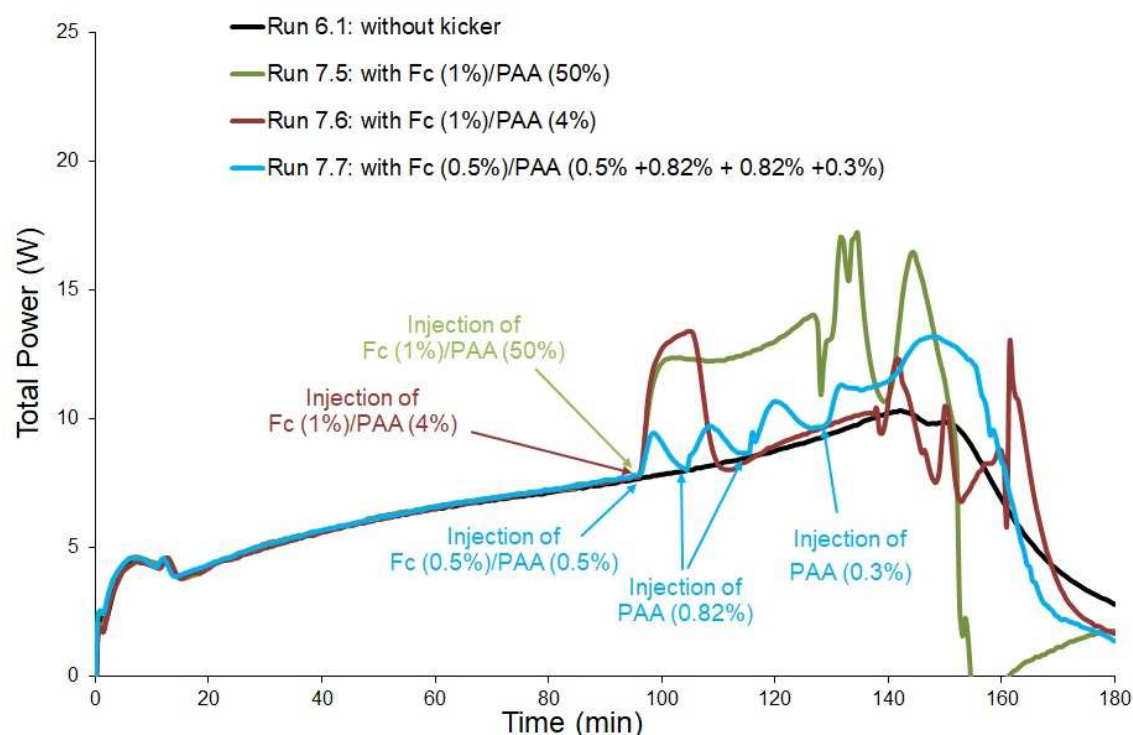
Industry is known to be interested in the final phase of the polymerization in terms of reaction rate after reaching the critical point  $X_f$ , as it is at this point that the rate begins to decrease gradually. It is thus highly desirable to increase the rate from that point by using a

kicker. As it is known, radical polymerization has the advantage of increasing its rate over time, by auto-acceleration [44-45], up to  $X_f$ , where the free liquid monomer phase disappears completely [46]. After this point, the monomer loses its mobility, and its free volume fraction along with its concentration decrease gradually with conversion, resulting in a dramatic reduction in the termination and propagation rates as well as the decomposition rate of peroxide, thus progressively slowing the polymerization rate over time [44,47]. In this regard, a series of experiments have been performed, which aimed to improve and accelerate the polymerization rate after the critical conversion  $X_f$ , using the inexpensive and industrially desirable PVA surfactant (Figure 5). Introducing the Fc/PAA (1/50 mol% vs. EHP) kicker (run 7.1, pink line, Fig. 5) at the critical conversion induced an immediate and strong polymerization activation, which proved too high for industrial scale implementation (typically a 110% excess of energy vs. the thermally induced reaction is accepted) [48]. Subsequently, the quantity of PAA was decreased with the aim to reduce this regeneration rate (runs 7.2-7.4, Fig. 5), but this failed to solve the problem: the energy released remained high even with only 1% PAA (run 7.4, light blue line Fig. 5). At this stage, the results indicated a fast EHP reduction and immediate Fc regeneration, resulting in the production of a large amount of EHP free radicals, even with a small amount of kicker. Considering that the control of the energy released by the polymerization will be more difficult at a time when it has reached its maximum, we explored other alternative approaches for the addition of the kicker, at earlier times and in the form of fractional additions, with aim to make the system more acceptable in terms of practical implementation.



**Fig. 5.** Heat-flow curves comparison of VCM polymerizations conducted at 53 °C using the Fc/PAA kicker (in mol% vs. EHP), EHP peroxide (1456 wt ppm vs. VCM) and PVAI surfactant (1000 wt ppm vs. VCM). VCM/H<sub>2</sub>O weight ratio = 50:50.

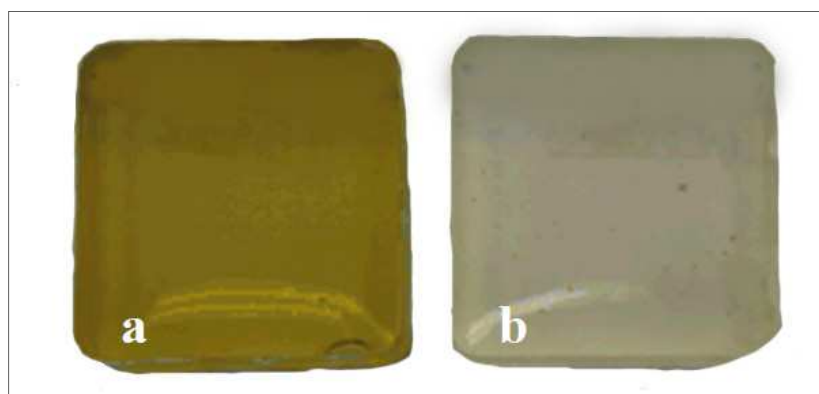
The introduction of the kicker was carried out, with PVA surfactant rather than the more expensive cellulosic Methocel® (run 6.6), at 40% conversion, which represents a point of stability at which the VCM droplets are stable against aggregation due to the formation of a PVC-PVA protective skin [49-52]. With Fc/PAA 1/50 mol% vs. EHP (run 7.5, green line, Fig. 6), an important activation of the polymerization during *ca.* 50 min and without any crust formation was obtained. Under these conditions, the 83% conversion was reached in 146 min in comparison to 177 min in absence of kicker for the same conversion. This gain in time can be considered as very important from an industrial point of view. Lowering the PAA amount to 4% (run 7.6, dark red line, Fig. 6), the activation was significant but less than previously, ending after a few minutes, likely due to the depletion of PAA amount. Upon addition of 0.5 % Fc/0.5% PAA and then successive additions of PAA (for a total of 2.5 mol% vs. EHP, run 7.7, blue line, Fig. 6), the gain in time to reach the 85% conversion was 16 min compared to the reference without kicker. Interestingly, this latter way of addition of PAA was not far from satisfactory in terms of respecting the 110% energy limits for industrial implementation.



**Fig. 6.** Heat-flow curves comparison of VCM polymerizations conducted at 53 °C using the Fc/PAA kicker (in mol% vs. n(EHP)), EHP peroxide (1456 wt ppm vs. VCM) and PVAI surfactant (1000 ppm). VCM/H<sub>2</sub>O weight ratio = 1/2 (50g/100g). In run 8.7, an extra amount of PVAI was added (500 ppm) at the 70% conversion.

SEC analyses of selected PVCs issued from our experiments showed that the macromolecular data were found very similar with or without the use of a kicker during their synthesis, at the final conversion (see SI section, Table S2), as already noticed in the case of PVAs (*vide supra*). Thermal tests were then performed on the PVC samples in order to check whether the presence of the kicker within the polymer impacted, as a first approximation, the thermal stability and thus the quality of the resulting material (details are given in the Experimental Section). Figure

7 shows the comparison of results obtained with the kicker-catalyzed polymerization (a, run 6.6) and a reference PVC issued from standard thermal-activated radical polymerization in suspension (b).



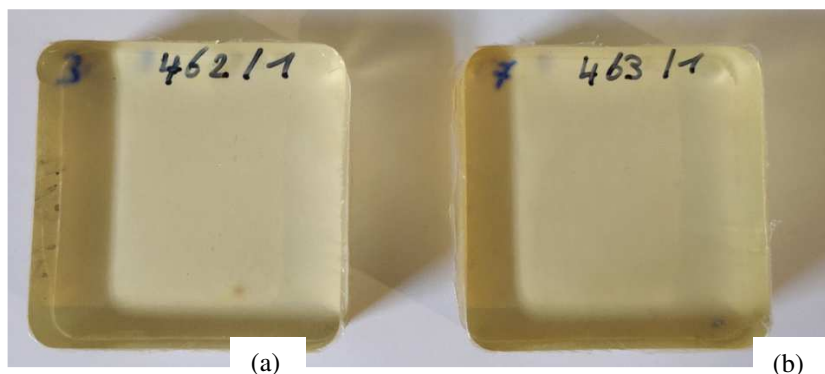
**Fig. 7.** Thermal stability test of (a): PVC produced with Fc/PAA (1/50 mol% vs. EHP, run 6.6), (b): PVC produced without kicker.

It is clear that the sample generated from run 6.6 was found to exhibit a poor thermal stability: it quickly turned yellow under heat compared to the reference that remained colorless. Such behavior upon heating may be due to chloride abstraction during the polymerization process, leading to the formation of unsaturations in the molecular backbone of the PVC that loses a part of its thermal stability [53,54]. Also, the presence of a significant amount of the oxidized form of PAA, up to 50 mol% vs. EHP in case of run 6.6, may possibly contribute to this yellowing at high temperatures [55,56].

In contrast, a couple of experiments done under industrial pilot conditions (Fig. S3, SI section; run 8.1 without kicker and run 8.2 with kicker Fc/PAA = 1/2.5 mol % vs. EHP) has proved to be worthwhile. In order to get closer to the CPA202 conditions with kicker injection shifted around  $X_f$ , the kicker was injected when the pressure was decreased by 0.5 bar after  $X_f$  and in the presence of a reduced amount of EHP peroxide (456 vs. 1456 ppm) as a high amount of energy release was observed under CPA202 conditions (runs 7.2, 7.3). With a reduced amount of PAA reductant of 2.5 mol% corresponding to run 7.7, to avoid possible thermal instability of formed PVC as in run 6.6 (see above, Fig. 7), a clear exothermic peak was observed at the injection of the kicker (Figure S3, SI section). When the polymerization was stopped at 375 min, almost 10% conversion was gained with the kicker (89%) as compared to the polymerization in absence of kicker (79%).

Finally, thermal tests performed on the PVC issued from run 8.2 revealed that this polymer exhibited an increase of melt color  $b^*$  of only one unit compared to the polymerization without kicker (8.1, Fig. S3), resulting in the absence of coloring of the PVC sample upon heat treatment (Figure 8). This minimal difference is likely due to the small amount of PAA used and can be considered as acceptable at an industrial level.





**Fig. 8.** Thermal stability test of (a): PVC produced without kicker (run 8.1) and (b): with ferrocene/AA (1/2.5 mol% vs. EHP, run 8.2).

## Conclusions

The above results show that the dual-component kicker activation of peroxides is a valuable tool for enhancing the polymerization rates of vinylic monomers such as vinyl acetate and vinyl chloride under suspension conditions. Whereas previous results using ferrocene derivatives as activators for the decomposition of peroxides mostly involved these reactants in stoichiometric amounts vs. peroxides, the use of suitable organic reductants to regenerate the activator allows the metal concentration in the reaction medium to be reduced to catalytic amounts, as low as 2.1 molar ppm, which is of prime interest from a synthetic point of view.

It must be emphasized, however, that generalizing a given activator/organic reductant to any vinylic substrate polymerization under such suspension conditions would be misleading. We clearly demonstrate here that the monomers assessed behave differently: the best kicker combination was found to be ferrocene/ascorbic acid for vinyl acetate, whereas vinyl chloride requires a combination of ferrocene/ascorbic acid palmitate ester to efficiently activate the decomposition of EHP peroxide. This is attributable to the tremendous complexity of these multiphase media, where several parameters must be carefully considered and adjusted, including, among others, the type of peroxide and surfactant, as the relative solubility and amphiphilic properties of the activator redox couple in action are factors that govern the overall reaction rate.

In addition, preliminary studies account for good efficiency of this kicker strategy towards the radical polymerization of methyl methacrylate as well.

Finally, although the final PVC materials did not completely match the physical requirements for practical PVC applications, we believe that ferrocene-based dual component kickers feature a valuable strategy to improve the global efficiency of radical polymerization processes under suspension conditions, which can be considered as a very important factor with regard to energy saving on an industry scale.

Clearly, the present study highlights the benefit of using ferrocene/reducing agent kicker as a worthwhile strategy for the polymerization in suspension of vinyl monomers at the industrial scale.

Further studies are in progress regarding the development of new generation kickers and will be published in a next future.

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## Author contributions

Yassir Zouhri: Investigation, Formal analysis, Visualization; Jean-Michel M. Berthé: Investigation, Formal analysis, Visualization; Fanny Bonnet: Supervision, Writing – review & editing, Visualization, Formal analysis; Bernard Stasik: Supervision; Christel Colemonts: Supervision, Formal analysis; Thierry Lasuye: Supervision, Project administration, Funding acquisition; André Mortreux: Conceptualization, Investigation, Supervision, Writing - Original Draft, Project administration, Funding acquisition; Yohan Champouret: Investigation, Supervision, Writing - Review and Editing, Visualization, Formal analysis, Funding acquisition; Marc Visseaux: Conceptualization, Investigation, Supervision, Writing – Original Draft, Writing – Review & Editing, Visualization, Project administration, Funding acquisition.

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