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# Synthesis of poly(vinyl alcohol) combs via MADIX/RAFT polymerization

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**Abstract**

Poly(vinyl acetate) combs have been prepared via macromolecular design via interchange of xanthate (MADIX)/reversible addition–fragmentation chain-transfer (RAFT) polymerization using xanthate functionalized polymer cores. The comb backbones were prepared using well-defined poly(vinyl alcohol) PVA polymers with a degree of polymerization of 20, 100 and 170, respectively. Functionalization with xanthates via R-group or a Z-group approach resulted in the formation of macromolecular MADIX agents. While Z group designed macromolecular xanthate agents appeared to inhibit the polymerization of vinyl acetate (VAc), R group designed macromolecular xanthate agents achieved to mediate efficiently the bulk polymerization of VAc affording PVAc combs. However, the growth of the combs was accompanied at low conversions by the formation of linear polymer chains as a result of the constant initiation (AIBN) and shoulders, which can be attributed to intermolecular coupling reactions. The proportions of single chains and termination products were observed to increase with the degree of polymerization of the macromolecular MADIX agents broadening the molecular weight distribution. As a result of a stable ester link between the branches and the PVA backbone, the branched PVAc architectures were finally hydrolyzed to afford poly(vinyl alcohol) combs.


*Keywords:* RAFT polymerization; Combs; Poly(vinyl alcohol)

## 1. Introduction

Over the past decade, the design of novel macromolecular architectures with well-defined structure has received substantial interest. Due to their interesting intrinsic properties (low bulk and solution viscosity, high functionality…), increasing research activity has been devoted to the preparation of branched polymers such as stars [1–8], combs [9–12] or dendrigrafts [13–16]. Because of the ease and the versatility of the free-radical process, the synthesis of branched polymers via living/controlled free radical polymerization techniques, i.e. nitroxide-mediated polymerization [17,18] (NMP), atom transfer radical polymerization [19,20] (ATRP) or reversible addition-fragmentation chain transfer [21–24] (RAFT) has been extensively investigated.

Among these free radical techniques, the MADIX/RAFT process appears to be particularly attractive since it can be successfully applied to the preparation of well-controlled polymers using a wide range of monomers.

Aiming at preparing narrow dispersed poly(vinyl alcohol) chains (PVA), a water-soluble, non-toxic and non-carcinogenic polymer with many biomedical applications [25–28], we recently started a research program on using RAFT chain transfer agents to synthesize well-defined poly(vinyl acetate) (PVAc), a precursor to PVA. We and others demonstrated the ability of xanthates to mediate efficiently the living radical polymerization of vinyl acetate (VAc) [29–31]. Narrow dispersed linear poly(vinyl acetate) chains up to 50 K were prepared in our laboratory. In further works, we reported the synthesis of well-defined three and four arms PVAc stars from multifunctional xanthate cores [5,6,32]. Two categories of multifunctional xanthate cores (R-group and Z-group

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approach) were designed to prepare PVAc stars via (1) the R-group approach and (2) the Z-group approach. The R-group approach attaching the xanthate functionality to the core via a fragmenting covalent bond was found to be suitable for preparing narrow-dispersed PVAc stars while the distribution of molecular weights tended to broaden via the Z-group approach (xanthate functionality attached to the core via a non-fragmenting covalent bond) due to the steric congestion and the decreased chain transfer activity between the linear macro-radical and the xanthate groups. Moreover, while the hydrolysis of the polymers prepared via Z-group approach resulted in the destruction of the architecture as the process also cleaved the xanthate linkage between the core and the arms, the hydrolysis of polymers prepared via the R-group approach afforded well-defined poly(vinyl alcohol) (PVA) star polymers.

In this paper, we describe an extension of the procedure leading to star polymers towards the preparation of well-defined poly(vinyl acetate) combs. We report here the synthesis, from narrow dispersed linear PVAc and subsequently well-defined linear PVA after hydrolysis, of two categories of xanthate functionalized polymer cores designed to synthesize well-defined polymer combs via a R-group or a Z-group approach (Scheme 1). The capacity of the synthetic approaches (R or Z) to provide a quantitative xanthate functionalization of the PVA backbone and the ability of the resulting polymeric cores to mediate the polymerization of VAc are discussed. The impact of the degree of polymerization of the xanthate functionalized polymer cores on the control of the polymerization of VAc is stressed.

## 2. Experimental part

### 2.1. Materials

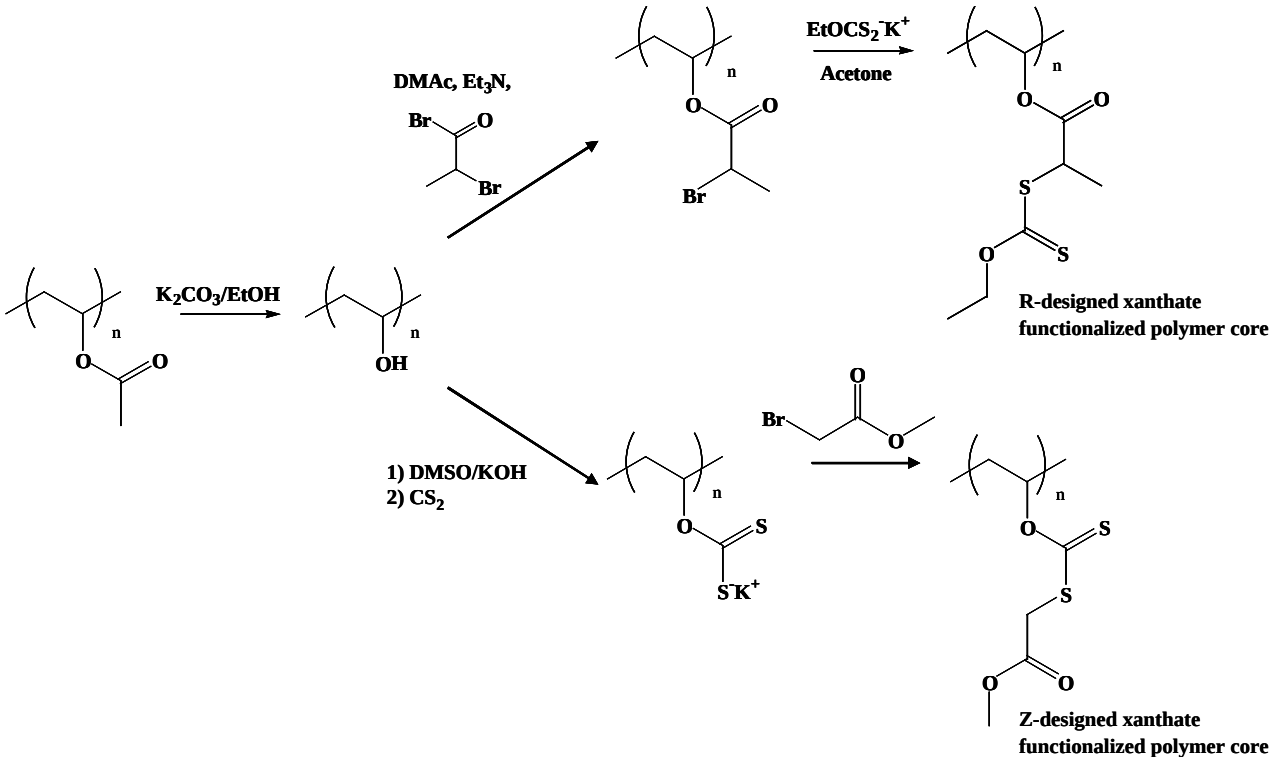
Potassium carbonate (Finechem Ajax, 95%), 2-bromopropionyl bromide (Aldrich, 97%), triethylamine (Aldrich, 99%), *O*-ethyl xanthic acid potassium salt (Aldrich), carbon disulfide (Aldrich, 99,9%), methyl bromoacetate (Aldrich, 97%) and trioxane (Aldrich, 99%) were used without further purification.

Dimethyl sulfoxide (DMSO), *N*,*N*-dimethylacetamide (DMAc), chloroform and acetone were obtained from Ajax FineChem (Australia) and were dried over activated molecular sieves (4 Å) before use. Methanol (Ajax FineChem) was used as received.

Vinyl acetate (VAc) (Aldrich, 99,9%), was filtered prior to passing through a column of basic aluminium oxide to remove inhibitors. 2,2′-Azobisisobutyronitrile (AIBN) (Aldrich, 99%) was recrystallized twice from ethanol.

### 2.2. Synthesis of methyl (ethoxycarbonothioyl)sulfanyl acetate

In a round-bottom flask, 5.24 g ($3.26\times10^{-2}$ mol) of the commercially available *O*-ethyl xanthic acid potassium salt was dissolved in 20 mL of dry acetone and 5 g ($3.26\times10^{-2}$ mol) of methyl bromoacetate was then added dropwise. The mixture was stirred at room temperature during 4 h. The white precipitate of KBr was isolated by filtration and acetone was evaporated off. Finally, the light green liquid product was purified by silica gel (Kiesigel-60) column chromatography (eluent: hexane/ethyl acetate 4/1 v/v). Yield: 95%.




Scheme 1. Synthetic approach to R- and Z-designed xanthate functionalized polymer cores.

### 2.3. Synthesis of the poly(vinyl acetate) precursors

Bulk polymerization of VAc was performed using 2,2′-azobisisobutyronitrile (AIBN) as the initiator and methyl (ethoxycarbonothioyl)sulfanyl acetate as chain transfer agent.

Typically, the polymerization of VAc (16 mL, $1.73\times10^{-1}$ mol) was carried out using AIBN (15 mg, $9.1\times10^{-5}$ mol), the functional xanthate agent (84.2 mg, $4.34\times10^{-4}$ mol) and trioxane (1.296 g, $1.44\times10^{-2}$ mol) as an internal reference for the measurement of VAc consumption as previously reported [29].

The solution was transferred to a Schlenk tube which was thoroughly deoxygenated by five consecutive freeze–pump–thaw cycles. The tube was then placed in a constant temperature water bath at 60 °C. The reaction was stopped by plunging the tube into iced water. The conversions were determined by $^1$H NMR in $CDCl_3$ by relative integration of vinyl (unreacted VAc) and $OCH_2$ (trioxane) protons.

After purification of the polymers, molecular weights of the linear PVAc were evaluated by $^1$H NMR in $CDCl_3$ from relative integration of the peaks *b* and *d* (Fig. 1(A)).

### 2.4. Hydrolysis of the poly(vinyl acetate) precursors

Two grams of PVAc ($2.32\times10^{-2}$ mol of vinyl acetate units) were dissolved in a vial with 20 mL of ethanol. Three grams of potassium carbonate ($2.17\times10^{-2}$ mol) were subsequently added in the solution. The vial was then placed in a water bath at 60 °C for 2 days.

### 2.5. Synthesis of R-designed xanthate functionalized polymer cores

In a first step, 0.5 g of PVA ($1.13\times10^{-2}$ mol of hydroxyl groups) was dissolved in 10 mL of dry DMAc. Triethylamine (1.22 g, $1.21\times10^{-2}$ mol, 1.1 equiv.) was then added. Bromopropionyl bromide (2.94 g, $1.36\times10^{-2}$ mol) was finally added dropwise at 0 °C during 3 h and the solution was stirred overnight at room temperature. After reaction, 100 mL of chloroform were added. The organic solution was then washed several times with an aqueous solution of sodium hydrogenocarbonate, several times with distilled water and dried over $MgSO_4$. The bromide functionalized polymer was precipitated several times in hexane until complete disappearance of the impurity peaks on the $^1$H NMR spectrum (Fig. 1(C)).

In a second step, the pure bromide functionalized polymer (0.5 g, $2.79\times10^{-3}$ mol) was reacted with the commercially available *O*-ethyl xanthic acid potassium salt (0.67 g, $4.18\times10^{-3}$ mol, 1.5 equiv.) during 3 h in dry acetone at room temperature. The insoluble white precipitate of KBr was filtered off and the solution was concentrated. The excess of xanthic acid salt was precipitated by adding chloroform and filtrated. The operation was repeated twice to ensure a complete elimination of the salt. Finally, the resulting polymer was precipitated several times in cold hexane (PVA20) or hexane/diethyl ether mixtures (PVA100 nd PVA200) and dried (see $^1$H NMR in Fig. 1(D)). Dried PVA-RAFT(R)-20 and

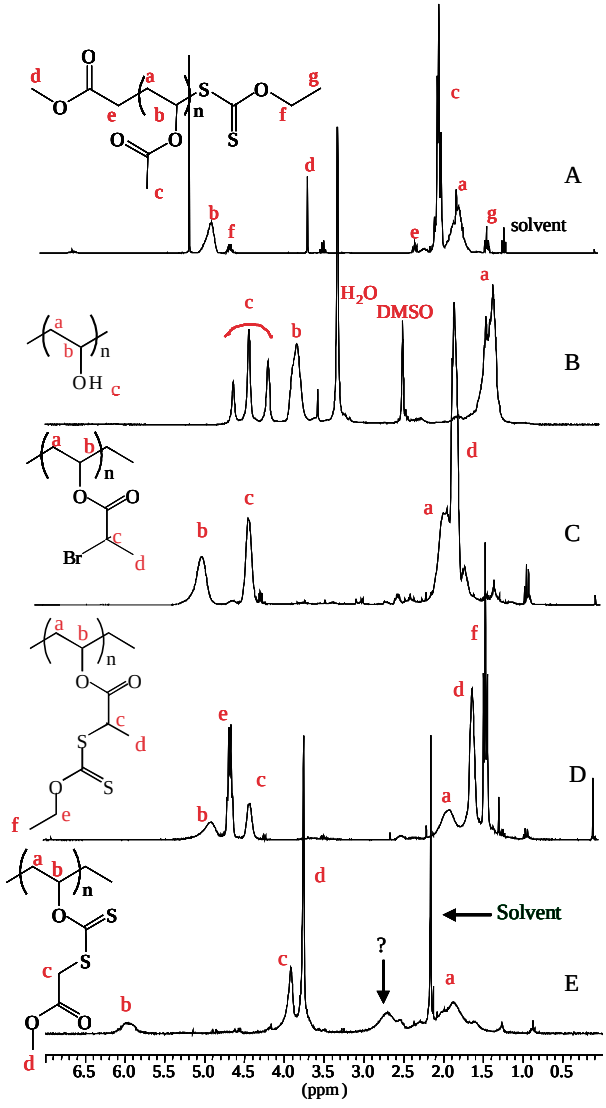



Fig. 1. Proton NMR spectra of PVAc (A), PVA (B), PVA-Br (C), PVA-RAFT(R) (D) and PVA-RAFT(Z) (E).

PVA-RAFT(R)-100 were stored at 4 °C. Due to increasing problems of solubility, PVA-RAFT(R)-200 was finally stored in solution (acetone) at 4 °C and dried just before use.

### 2.6. Synthesis of Z-designed xanthate functionalized polymer cores

0.5 g of PVA ($1.13\times10^{-2}$ mol of hydroxyl groups) was dissolved in 15 mL of DMSO at 40 °C. A low volume of an aqueous solution of KOH (0.95 g, $1.69\times10^{-2}$ mol, 1.5 equiv in regard to hydroxyl groups) was added at room temperature. A large excess of carbon disulfide (6.8 mL, $1.13\times10^{-1}$ mol, 10 equiv) was then slowly added at 0 °C during 30 min. The dark red solution was stirred during 2 h at room temperature. Finally, methyl bromoacetate (MBA) (2.59 g, $1.69\times10^{-2}$ mol, 1.5 equiv.) was slowly added during 1 h at room temperature. The resulting yellow solution was stirred overnight.

After reaction, 100 mL of diethyl ether was added. The organic phase was washed several times with water, dried with magnesium sulphate and filtered. The solution was concentrated and the polymer was precipitated several times in cold hexane (see $^1$H NMR in Fig. 1(E)).

### 2.7. Synthesis of PVAc combs

Bulk polymerizations of VAc were performed using 2,2′-azobisisobutyronitrile (AIBN) as the initiator and the R-designed xanthate functionalized polymer cores given in Scheme 1 as chain transfer agent ($1.1\times10^{-2}$ mol L$^{-1}$ of xanthate functions).

Typically, the polymerization of VAc (3 mL, $3.25\times10^{-2}$ mol) was carried out using AIBN (1.1 mg, $6.7\times10^{-6}$ mol), the functional xanthate agent (7.3 mg of polymer, $3.3\times10^{-5}$ mol of xanthate functions) and trioxane (243 mg, $2.7\times10^{-3}$ mol) as an internal reference for the measurement of VAc consumption as previously reported [29].

The stock solution was transferred to Schlenk tubes which were thoroughly deoxygenated by five consecutive freeze–pump–thaw cycles. The tubes were then placed in a constant temperature water bath at 60 °C and were removed at regular time intervals. The reactions were stopped by plunging the tubes into iced water. The conversions were determined by $^1$H NMR in $CDCl_3$ by relative integration of vinyl (unreacted VAc) and $OCH_2$ (trioxane) protons.

### 2.8. Hydrolysis of PVAc combs

One gram of PVAc ($1.16\times10^{-2}$ mol of vinyl acetate units) was dissolved in a vial with 10 mL of ethanol. 1.5 g of potassium carbonate ($1.09\times10^{-2}$ mol) was subsequently added in the solution. The vial was then placed in a water bath at 60 °C for 2 days.

### 2.9. Characterization

$^1$H NMR spectra were recorded on a Bruker spectrometer (300 MHz) using $CDCl_3$ as solvent for PVAc materials and $D_2O$ for PVA polymers. Gel permeation chromatography (GPC) analysis of PVAc polymers were performed in THF at 25 °C (flow rate: 1 mL min$^{-1}$) using a Shimadzu modular system comprising an auto-injector, a Polymer Laboratories 5.0 μm bead-size guard column (50×7.5 mm) followed by four linear PL columns ($10^6$, $10^5$, $10^4$ and $10^3$ Å) and a differential refractive index detector.

GPC analysis of PVA polymers were performed in *N*,*N*-dimethylacetamide (DMAc) (0.03% w/v LiBr, 0.05% BHT) at 40 °C (flow rate: 1 mL min$^{-1}$) using a Shimadzu modular system comprising a SIL-10AD auto-injector, a Polymer Laboratories 5.0 μm bead-size guard column (50×7.8 mm) followed by four linear PL columns ($10^5$, $10^4$, $10^3$ and 500 Å) and a RID-10A differential refractive index detector. Calibration of the GPCs was performed with narrow polydispersity polystyrene standards ranging from 500 to $10^6$ g/mol. The experimental molecular weights were corrected for PVAc using the Mark–Houwink parameters (universal calibration): $K=16\times10^{-5}$ mL g$^{-1}$ and $\alpha=0.70$ (PS, $K=14.1\times10^{-5}$ mL g$^{-1}$ and $\alpha=0.70$).

Absolute molecular weights were determined by GPC (Polymer Laboratories columns (PLgel guard 3 μm 50×7.5 mm followed by 2 PLgel Mixed C 5 μm 300×5 mm), DMAc with 0.03% w/v LiBr and 0.05% w/v BTH at 50 °C, flow rate = 0.75 mL min$^{-1}$) on a Shimadzu apparatus equipped with refractive index (RID-10A) and laser light scattering detection (precision detectors PD2100, $\lambda=683$ nm).

## 3. Results and discussion

### 3.1. Synthesis of the R and Z designed xanthate functionalized polymer cores

R and Z designed xanthate functionalized polymer cores have been prepared from linear poly(vinyl alcohol) (Scheme 1). The strategy required the presynthesis of well-defined PVAc precursors via MADIX polymerization in the presence of methyl (ethoxycarbonothioyl)sulfanyl acetate. A series of linear precursors with degree of polymerization ($\overline{DP}_n$) ranging from 20 to 170 was thus prepared aiming at evaluating the influence of the polymer core chain length on the control of the polymerization of the combs. The main characteristics of the PVAc precursors are collected in Table 1. The conversions of VAc were calculated by $^1$H NMR in $CDCl_3$ from the relative integrations of $CH_2$ protons of the internal reference (trioxane) and of the vinyl protons of the monomer as previously reported [29]. Due to the controlled character of the polymerization, the polydispersity of the PVAc chains remained low (PDI ≤ 1.4) and the experimental molecular weights evaluated from GPC and $^1$H NMR were in good agreement. The PVAc chains were subsequently hydrolyzed under mild conditions (EtOH/$K_2CO_3$) to afford well defined linear poly(vinyl alcohol). The complete hydrolysis of the acetate functionality was confirmed by the total disappearance ($^1$H NMR spectrum in $D_2O$) of the peak corresponding to $CO_2CH_3$ groups and the shifting of the peak corresponding to $CH_2$–C*H*– protons located on the polymer backbone (Fig. 1(B)). Surprisingly, the molecular weights (MW) of the resulting polymers determined by GPC (in DMAc) tended to be much higher than the MW of the PVAc precursors. These divergent theoretical and experimental PVA MW data could suggest chain–chain coupling reactions (S–S bonds) involving the thiol chain ends formed from the cleavage of the xanthate ω-end-group under basic conditions. However, no double MW population could be detected by LC–MS analysis (not shown) of hydrolyzed PVA. At this stage we believe this trend to be a consequence of the change of

Table 1
Main characteristics of the PVAc precursors

| Precursor | $\overline{DP}_n$ ($^1$H NMR) | $\overline{DP}_n$ (GPC in THF) | PDI |
|---|---|---|---|
| PVAc-20 | 20 | 35 | 1.23 |
| PVAc-100 | 99 | 97 | 1.34 |
| PVAc-200 | 169 | 154 | 1.35 |

Table 2
Main characteristics of the R- and Z-designed xanthate functionalized polymer cores

| Polymer | $\overline{M}_n$ (GPC) | PDI |
|---|---|---|
| PVA-20 | 9700[a] | 1.24 |
| PVA-RAFT(R)-20 | 6100[b] | 1.40 |
| PVA-RAFT(Z)-20 | 8400[b] | 1.41 |
| PVA-100 | 27,200[a] | 1.37 |
| PVA-RAFT(R)-100 | 8100[b] | 1.38 |
| PVA-200 | 48,900[a] | 1.37 |
| PVA-RAFT(R)-200 | 23,200[b] | 1.51 |

[a] GPC analysis performed in DMAc.
[b] GPC analysis performed in THF.

hydrodynamic volume and the poor solubility of PVA in DMAc. The hydrolysis was accompanied by a slight broadening of the polydispersity (Table 2). The hydroxyl groups of the PVA backbones were then functionalized with R or Z designed xanthate transfer agents applying similar strategies as described in our previous paper [6] (Scheme 1). The main characteristics of the resulting xanthate functionalized polymers (PVA-RAFT(R)-20, PVA-RAFT(Z)-20, PVA-RAFT(R)-100 and PVA-RAFT(R)-200) are collected in Table 2.

Applying the 2-steps R approach strategy, R designed xanthate transfer agents were successfully prepared. The quantitative modification of the PVA was confirmed by $^1$H NMR, by the total disappearance of the peaks corresponding to hydroxyl protons (peaks *c* of PVA; $\delta = 4.17$, 4.43 and 4.63 ppm), the shift of the peaks corresponding to –*CH*$_2$–CH–O (from $\delta = 1.34$–1.85 ppm) and –CH$_2$–*CH*–O protons (from $\delta = 3.81$ to 4.88 ppm) and the appearance of new peaks corresponding to the introduction of xanthate groups (Fig. 1(D)). R designed xanthate functionalized polymer cores of high purity were finally obtained after tedious selective precipitation procedures.

In contrast, the anchorage of pendent xanthate groups on PVA via the Z approach strategy resulted in partial functionalization of the polymer backbone as suggested by $^1$H and $^{13}$C NMR spectra (not shown). Although the majority of the hydroxyl functions along the backbone was effectively transformed into the expected xanthate groups, (Fig. 1(E)), the ($^1$H and $^{13}$C) NMR analysis of purified Z designed xanthate functionalized polymer cores (same procedure of purification) revealed a broad non-attributed peak ($\delta = 2.72$ ppm) as well as the presence of two distinct kinds of thiocarbonyl groups around 210 ppm (see Supporting Information) which may reflect the formation of an impurity during the one pot procedure, the occurrence of unexpected side reactions affecting the backbone functionalization or the presence of unreacted xanthic acid potassium groups on the backbone.

The introduction of xanthate groups (R or Z) had drastic consequences on the solubility of the polymers, which finally appeared to be exclusively soluble in organic solvents. It is worth noting that Z designed xanthate functionalized polymer cores were not soluble in vinyl acetate and consequently not suitable for the bulk polymerization of VAc. This phenomenon may be a consequence of the presence of unreacted xanthic acid potassium groups along the backbone. Except PVA-RAFT(R)-200 which presented limited solubility in VAc after storage, R designed xanthate functionalized polymers were easily dissolved in VAc.

The chemical modification of the PVA was shown to have little or no influence on the polydispersity of the resulting polymers (Table 2).

### 3.2. Preparation of PVAc combs

Due to the non-solubility of Z designed xanthate functionalized polymer cores in vinyl acetate, the polymerization of VAc mediated by the macromolecular Z designed xanthate agents was studied in freshly distilled dioxane in the presence of AIBN. After 5 days at 60 °C, no polymerization was observed indicating very long inhibition periods.

Considering the important efforts devoted to the purification of the Z designed xanthate functionalized polymer cores by precipitation, the presence of impurities within the polymer cores combined with the extreme sensitivity of the living radical polymerization of vinyl acetate [6,29] are likely responsible for the failure of VAc polymerization.

Contrary to Z designed xanthate functionalized polymer cores, the R designed xanthate functionalized polymer cores were suitable for the synthesis of PVAc combs. The preparation of PVAc combs was investigated in bulk at a constant concentration of xanthate functionality ($1.1\times10^{-2}$ mol L$^{-1}$) at 60 °C in the presence of AIBN ($2.2\times10^{-3}$ mol L$^{-1}$). Conversion versus time plots for the bulk polymerization of VAc mediated with PVA-RAFT(R)-20, PVA-RAFT(R)-100 and PVA-RAFT(R)-200 re given in Fig. 2. Inhibition periods varying from 30 min for PVA-RAFT(R)-20 and PVA-RAFT(R)-200 to 1 h for PVA-RAFT(R)-100 were observed. These inhibition periods are probably related to the presence of trace levels of impurity combined with the extreme sensitivity of the living radical polymerization of VAc [29]. Post-inhibition, the kinetics were consistent with a constant concentration of radicals. The polymerization of VAc was quite fast (~70% of conversion in 5 h 30+30 min of inhibition in presence of

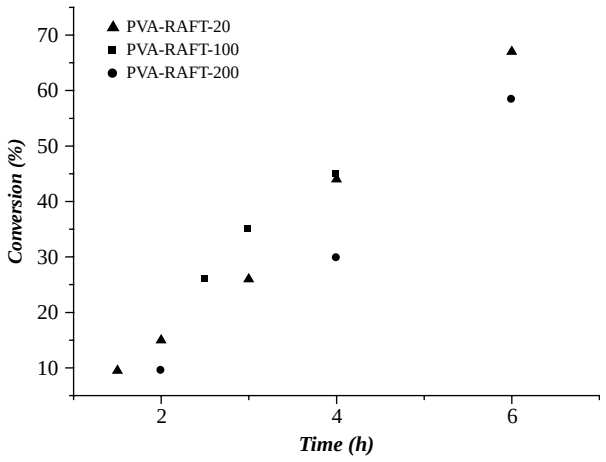
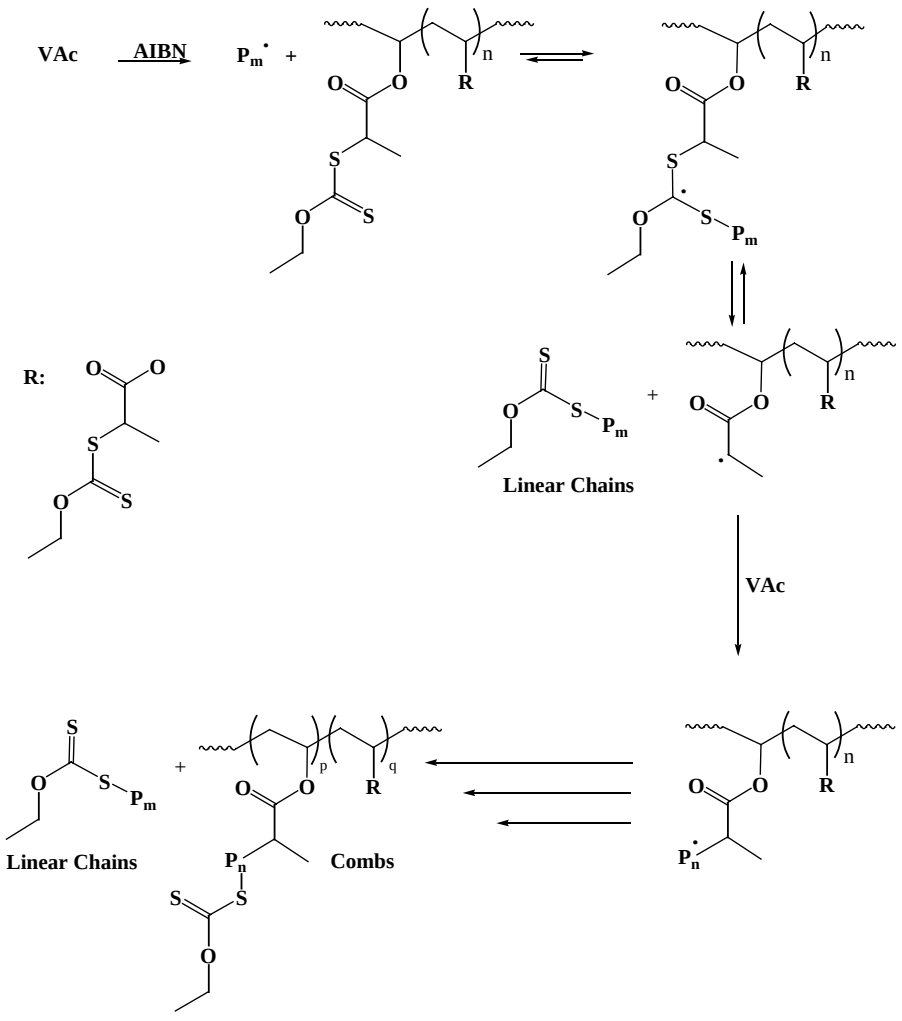



Fig. 2. Conversion vs time plots obtained by proton NMR for the bulk polymerization of VAc at 60 °C with [Xanthate] = $1.1\times10^{-2}$ mol L$^{-1}$ and [AIBN] = $2.2\times10^{-3}$ mol L$^{-1}$.

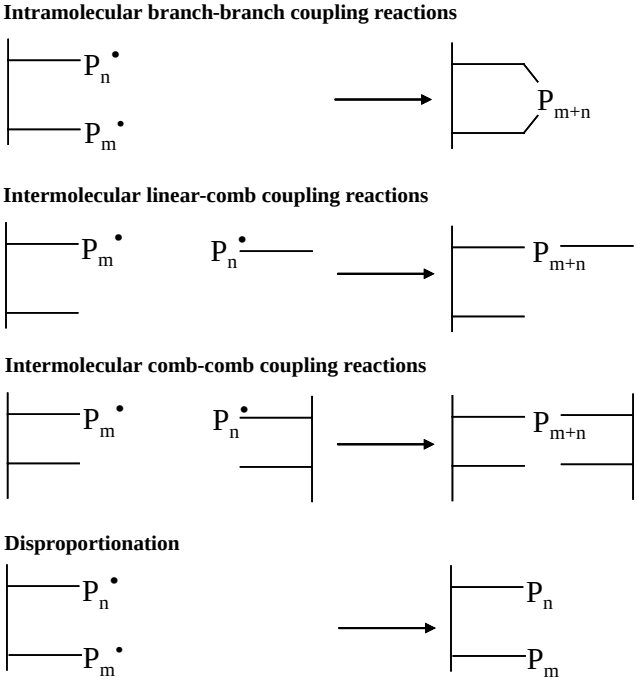



Scheme 2. RAFT process.

PVA-RAFT(R)-20) though slightly lower than the rates previously observed in the presence of trifunctional or tetrafunctional R designed xanthate agents (~80% in 4 h 20+1 h of inhibition) [29].

As shown in Scheme 2, in the presence of R designed functionalized polymer cores, two types of active propagating species coexist in solution, those located on the PVA backbone and the linear macroradicals resulting from AIBN initiation. The propagating species can terminate via intermolecular, intramolecular radical–radical coupling reactions or disproportionation reactions [33] leading to the formation of combs with dead branches, comb–comb polymers and dead linear chains (Scheme 3) and RAFT-functionalized linear chains are eventually generated during the process. This scenario has been observed earlier in the synthesis of polystyrene stars using the R-group method [34] and has been quantitatively predicated via a modeling approach [35].

Typical GPC chromatograms are given in Fig. 3. As expected theoretically, the GPC traces (THF) exhibited two peaks, one at high molecular weights that was clearly attributed to the growth of combs from R designed xanthate functionalized polymer cores and the second to low molecular weights that reflected the presence of linear




Scheme 3. Fate of the macroradicals located on the combs.

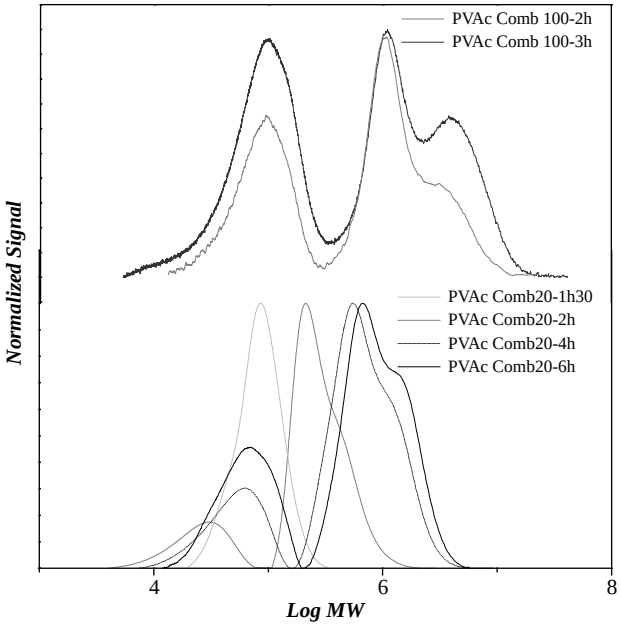



Fig. 3. Evolution of GPC chromatograms for the RAFT bulk polymerization of VAc at 60 °C in the presence of PVA-RAFT(R)-20 and PVA-RAFT(R)-100.

chains. The ratio (linear chains/combs) rose steadily with time as a consequence of the continuous initiation. It is worth noting that this ratio increased with the degree of polymerization of the xanthate functionalized polymer cores. This trend may be the consequence of termination events occurring on the PVA c back bone or the preferred growth of linear chains compared to comb branches due to steric hindrance. The molecular weights of the two populations (combs and linear chains) evolved gradually with conversion (Table 3). However, the peaks corresponding to the comb polymers displayed high molecular weights shoulders at low or moderate conversions ($\geq 10\%$) which are indicative of intermolecular radical–radical termination events. The intermolecular coupling reactions were more prominent at high conversions of VAc leading to a significant broadening of the molecular weight distribution of the combs (PDI = 1.46 at 67% conversion and PDI = 1.97 at 45% conversion, respectively, in presence of PVA-RAFT(R)-20 and PVA-RAFT(R)-100). Interestingly the prominence of the radical–radical coupling reactions seemed to be amplified with the degree of polymerization of the xanthate functionalized polymer core (Fig. 3). The increase in coupling products with increasing conversion is directly correlated with the total amount of radicals released into the polymerization system over time. Such behavior—while operational in any RAFT polymerization—can be especially pronounced in RAFT R-group polymerizations and will be the subject of a forthcoming theoretical study.

The theoretical MW of the growing PVAc branches, evaluated from conversion with the following equation:

$\bar{M}_{n\ th} = 0.86 \times R \times \text{Conversion} + m_{xanthate}$ with $R = [\text{VAc}]_0/[\text{xanthate}]_0$, conversion in percent and $m_{xanthate}$ molecular mass of the macroRAFT agent, were lower than the MW of the linear chains determined by GPC (Table 3). The non-agreement between these two values could confirm the preferred growth of linear chains due to decreased accessibility of the xanthate groups (Table 3).

Finally, absolute MW of the PVAc combs were measured by static light scattering (SLS) in DMAc. Absolute MWs appeared to deviate significantly from the theoretical values calculated from the conversion of VAc (Table 3). The difference between theoretical and experimental MW determined by SLS corroborated the presence of double molecular weight comb–comb structures.

As previously described [5,6], the poly(vinyl acetate) combs were finally hydrolyzed under soft hydrolysis conditions. The presence of a stable ester linkage between the branches and the PVA backbone allowed the hydrolysis of the poly(vinyl acetate) branched polymers maintaining the comb architecture giving birth to poly(vinyl alcohol) combs.

Table 3
Molecular weight/conversion data for PVAc combs

| Polymer | PVA-RAFT(R)-X | Conv% | $\bar{M}_{nth\ branch}$ [a] ($\times 10^{-3}$ g mol$^{-1}$) | $\bar{M}_{n\ linear\ chains}$ [b] ($\times 10^{-3}$ g mol$^{-1}$) | $\bar{M}_{nth\ comb}$ [a] ($\times 10^{-5}$ g mol$^{-1}$) | $\bar{M}_{n\ comb}$ [c] ($\times 10^{-5}$ g mol$^{-1}$) | $\bar{M}_{n\ GPC}$ ($\times 10^{-5}$ g mol$^{-1}$) | PDI[d] |
|---|---|---|---|---|---|---|---|---|
| Comb 1 | 20 | 9 | 7.9 | N.d. | 1.6 | N.d. | 0.75 | 1.21 |
| Comb 2 | 20 | 15 | 13 | 21 (0.62)[e] | 2.6 | 5.5 | 2.1 | 1.19 |
| Comb 3 | 20 | 26 | 22.2 | 30.1 (0.74)[e] | 4.5 | 7.1 | 3.1 | 1.26 |
| Comb 4 | 20 | 44 | 37.5 | 43.3 (0.87)[e] | 7.7 | 11 | 4.7 | 1.35 |
| Comb 5 | 20 | 67 | 56.7 | 55.6 (1.02)[e] | 11.7 | 14 | 6.1 | 1.46 |
| Comb 6 | 100 | 26 | 22.2 | 39.5 (0.56)[e] | 22.7 | N.d. | 9.8 | 1.48 |
| Comb 7 | 100 | 35 | 29.7 | 41.2 (0.72)[e] | 30.5 | N.d. | 10.4 | 1.77 |
| Comb 8 | 100 | 45 | 38.2 | 52.4 (0.73)[e] | 39 | N.d. | 13.8 | 1.97 |
| Comb 9 | 200 | 9.5 | 8 | 14.4 (0.55)[e] | 14 | N.d. | 3.2 | 12[f] |
| Comb 10 | 200 | 29.8 | 25.2 | 50.4 (0.5)[e] | 44 | N.d. | 19.3 | 7.4[f] |
| Comb 11 | 200 | 58.4 | 49.4 | 77.2 (0.64)[e] | 86 | N.d. | 4.4 | 1.43 |

[a] Determined from $^1$H NMR ($CDCl_3$).
[b] Determined from SEC (THF).
[c] Determined from PDI and $\bar{M}_w$ (SLS).
[d] Analysis of the comb excluding the contribution of linear chains.
[e] Ratio $\bar{M}_{n\ th\ branch}/\bar{M}_{n\ linear\ chains}$.
[f] Results affected by the formation of aggregates.

## 4. Conclusions

Poly(vinyl acetate) combs were elaborated using xanthate functionalized polymer cores. Contrary to the Z designed macromolecular xanthate agents which were shown to inhibit the polymerization of VAc owing to the presence of impurities within the polymer cores, xanthate functionalized polymers obtained via the R approach were suitable for the synthesis of PVAc comb polymers. However, the comb distributions were accompanied at low or moderate conversions by a linear polymer chains distribution and shoulders at high molecular weights which can be attributed to radical–radical termination events. The branched polymers were subsequently successfully hydrolyzed giving birth to poly(vinyl alcohol) combs.

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## Supplementary data

Supplementary data associated with this article can be found at doi:10.1016/j.polymer.2005.12.004

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