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Preparation of New Multiarmed RAFT Agents for the Mediation of Vinyl Acetate Polymerization

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Summary: In this study five xanthate (Reversible Addition-Fragmentation chain Transfer (RAFT)/Macromolecular Design through Interchange of Xanthates (MADIX)) agents were synthesized, namely monofunctional, difunctional, trifunctional and tetrafunctional species of the form S=C(O-Z)-S-R, with different leaving groups and different activating moieties some of which are completely novel. Polyvinyl acetates (PVAc) in the form of linear, three armed and four armed star shaped polymers were then successfully synthesized in reactions mediated by these xanthate RAFT/MADIX agents.

Keywords: chain transfer; living polymerization; mediation; radical polymerization; RAFT

Introduction

Living/controlled free radical polymerization processes have drawn significant attention from both the industrial and academic fields.[1] In the last decade, considerable effort has been spent to develop free radical processes that display the characteristics of living polymerization.[2–4] This research area has become one of the most rapidly growing areas of polymer chemistry.

Through the use of living radical polymerization techniques one is able to maintain the advantages of conventional free radical polymerization, such as being compatible with a wide range of vinyl monomers and insensitivity to small trace of impurities, while minimizing the disadvantages such as producing polymers with a wide molar mass distribution.

Living free radical polymerization is a viable route to obtain polymers with narrow polydispersity (PDI), and controlled molar mass under simple reaction conditions.[3–7]

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Living radical polymerization also offers control over the chain-ends of the synthesized polymer and most importantly gives polymer products that can be reactivated for chain extension with either the same or another monomer opening the way to the synthesis of block copolymers and other more complex architectures.[6]

In the past block copolymer formation was only possible by means of living ionic polymerization techniques, which require stringent reaction conditions such as high vacuum, inert atmosphere, absence of impurities, and are limited to a relatively small number of monomers.[8]

Living free radical polymerization allows a wide variety of existing as well as totally new polymer systems with accurately known structures to be designed and synthesized.

Several Living Free Radical Polymerization (LFRP) techniques have been developed over the past decade and all of them are based either on a reversible end capping technique such as Atom Transfer Radical Polymerization (ATRP)[7,9] and Stable Free Radical Polymerization (SFRP),[7,10] or a reversible transfer technique such as degenerative transfer with alkyl iodides. In all of the techniques the exchange between dormant and active species is fast

relative to propagation, and the percentage of terminated chains is small.[1]

In 1998 Rizzardo et al.[7,11–16] reported a new controlled free radical polymerization technique that is applicable to a vast range of monomer types while being elementary to implement; it is based on reversible addition-fragmentation chain transfer and is designated the RAFT process. The RAFT process has become one of the most rapidly developing areas of polymer science.[17] This can be ascribed to the ease in which chain length, architecture, composition and functionalities of various polymers and copolymers can be prepared under conditions similar to those employed in conventional free radical polymerization (monomers, initiators, solvents and temperature).

Vinyl acetate can only be polymerized via a radical mechanism[18] and is a typical example of a monomer that cannot easily be polymerized using NMP or ATRP.[18,19] Vinyl acetate is a widely used monomer in the adhesives, paints, and concrete additives industries.[20,21] Vinyl acetate is a precursor in the synthesis of polyvinyl alcohol, which has applications in a pharmaceutical industry as well as in paper making and adhesives.[22] The controlled free radical polymerization of vinyl acetate is of particular technological interest.

In the case of RAFT mediated polymerization, dithiocarbonate and trithiocarbonate inhibit the polymerization of vinyl acetate as the vinyl acetate propagating radical is a poor homolytic leaving group and the fragmentation of the RAFT adduct radical is therefore very slow.[19]

Wakiota et al.[18] succeeded in controlling the polymerization of vinyl acetate by using an iron (I) complex. Controlled polymerization of vinyl acetate has also been achieved using either dithiocarbamates or xanthates as RAFT agents.[23,24] The ability of these compounds to control vinyl acetate polymerization can be correlated to an increase in the electron density at the radical centre i.e. the intermediate macro RAFT radical, which destabilizes the RAFT-adduct radical hence increasing the fragmentation rate.[19,25]

The present study aims at extending the available database of xanthate RAFT agents that might be used to control free radical polymerization of vinyl acetate.

Chemicals

The following reagents were used:

Potassium hydroxide 85% (SAARchem), 1,4 butandiol 99% (Acros), carbon disulfide 99.5% (Merck), 2-bromopropionic acid 99% (Aldrich), hydrochloric acid 32% (Merck), magnesium sulphate (anhydrous) 62–70% (Merck), pentaerythitol 98% (Merck), 1,1,1 tris(hydroxymethyl)ethane 98% (Fluka), ethyl 2-bromo propionate 99% (Aldrich), THF (Sigma-Aldrich, distilled from LiAlH4), Acetone 99.5% (SAARchem), diethyl ether 99.5% (Merck), ethanol 99.8% (Sigma-Aldrich), acetonitrile 99.9% (Aldrich), sodium carbonate 99.5% (Sigma), zinc chloride (Merck), ortho-phosphoric acid 85% (Fluka), D(+) glucose anhydrous (Associated Chemical Enterprises (PTY) Ltd), sodium metal (SAARchem), 2,2 azobis(isobutyronitrile) (AIBN; Riedel de Haen) was recrystallized from methanol. Polystyrene 1% crosslinked with divinylbenzene (Stratospheres®).

Analysis

The synthesized xanthate RAFT agents were characterized by nuclear magnetic resonance (NMR) spectroscopy, fourier-transform infrared spectroscopy (FT-IR) and ultraviolet spectroscopy (UV). The molar masses of the polymers were determined with size exclusion chromatography.

Nuclear Magnetic Resonance Spectroscopy (NMR)

Proton ^{1}H-NMR and carbon ^{13}C-NMR spectra of the xanthate RAFT agents were obtained by using a Varian VXR 300 M equipped with a Varian magnet (7.0 T), and 600 MHz Varian unity Inova spectrometer equipped with an Oxford magnet (14.09T). Deuterated chloroform ($CDCl_3$) and deuterated methyl sulfoxide (DMSO) were used as solvents, depending on the solubiity of the synthesized xanthate RAFT agents.

All spectra were referenced to tetramethylsilane (TMS) at 0 ppm.

Fourier-Transform Infrared Spectroscopy (FTIR)

The infrared spectra were recorded using a Perkin Elmer Paragon 1000 FT-IR with a photoacoustic cell (PAS), which has the advantage that sample preparation is eliminated and a sample can be scanned in whatever form it appears. The sample was placed in an MTEC 300 chamber which was flushed with ultra-high-purity helium.

Ultraviolet/Visible Spectrometer

A Perkin Elmer UV/visible spectrometer Lambda 20 Spectrometer was used to identify the UV absorption band of the C=S bond in the structure of the RAFT agents. The data was analyzed with UVWinlab v.4.2 software. Quartz cuvettes (supplied by CND Scientific) with a 10 mm path length were used.

Size Exclusion Chromatography (SEC)

The molar masses were determined with size exclusion chromatography. The SEC instrument consisted of a Waters 117 plus Auto-sampler, Waters 600 E system Controller (run by Millennium[32] V 3.05 software) and a Waters 610 fluid unit. A Waters 410 differential refractometer and Waters 2487 dual wavelength absorbance detector were used at 30 °C as detector. THF (HPLC grade) sparged with IR grade helium was used as eluent at a flow rate of 1 mL/min. the column oven was kept at 30 °C and the injection volume was 100-μL. Two PLgel 5-μm Mixed-C columns and a pre-column (PLgel 50-μm Guard) were used. The system was calibrated with narrow polystyrene standards ranging from 800 to 2×10^6 g/mol. All molar masses were reported as polystyrene equivalents.

Multi-Angle Laser Light Scattring (MALLS)

The molar masses of the star polymers were also determined using Multi-Angle Laser Light Scattering (MALLS), the chromatograph used consisted of a 610 Waters pump, a 717 autosampler (Waters, Milford, MA), a laser photometer miniDAWN (Wyatt Technology Corporation, Santa Barbara, CA) and a 410 differential refractometer (Waters). ASTRA software (Wyatt Technology Corporation) was used for data collection and processing.

Experimental Part

Synthesis of S-sec propionic acid O-ethyl xanthate (monofunctional) RAFT agent (1)

Potassium hydroxide pellets (21 g, 0.375 mol), ethanol (60 g, 76 mL) and a stirrer bar were placed in a 250-mL round-bottomed flask fitted with a reflux condenser. The mixture was heated under reflux for one hour. After cooling in an ice bath, carbon disulphide (28.5g, 22.6 mL, 0.375 mol) was added slowly resulting in an almost solid mass. The crystals were filtered off and washed with three 20 mL portions of ether. The solid potassium O-ethyl dithiocarbonate product was then recrystallized from absolute ethanol (yield was 41 g, 68%).

Potassium O-ethyl dithiocarbonate (8.3 g, 0.052 mol) was then dissolved in 30 mL ethanol in a 250-mL round-bottomed flask. The reaction mixture was stirred overnight with 2-bromopropionic acid (7.95 g, 4.67 mL, 0.052 mol), which had been neutralized by the addition of sodium carbonate (0.026 mol, 2.75 g). The mixture was then acidified by the dropwise addition of 1 M hydrochloric acid, and extracted with 50 mL ether and the ether layer washed with 20 mL distilled water. After drying over magnesium sulphate (anhydrous) the solvent was evaporated. The residue was cooled in order to form crystals and the product was recrystallized from hexane. A white crystalline solid (3 g, 30% yield) was obtained (m.p 45–47 °C).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 1.38 (t, 3H, **CH_3**–CH_2–, $J_{CH3–CH2–} = 7.1$ Hz), 1.56 (d, 3H, **CH_3**–CH–, $J_{CH3–CH–} = 7.4$ Hz), 4.39 (q, 1H, CH_3–**CH**–, $J_{CH3–CH–} = 7.4$ Hz), 4.62 (q, 2H, CH_3–**CH_2**–, $J_{CH3–CH2–} = 7.1$ Hz).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 13.3 (**CH_3**–CH_2–), 16.2 (**CH_3**–CH–), 46.7 (CH_3–**CH–**), 70.4 (CH_3–**CH_2**–), 178.1 (C=O), 211.9 (C=S).

FT-IR (photoacoustic cell) PAS (cm^{-1}) wavenumbers and their assignments: 3518 (–OH), 2980 (–CH_2–, –CH_3), 1724 (C=O), 1265 (C–O), 1048 (C=S), 862 (C–S).

UV(C=S): ($n \rightarrow \pi^*$, $\lambda_{max} = 354$ nm L) and ($\pi \rightarrow \pi^*$, $\lambda = 278$ nm). Acetonitrile was used as solvent.

Synthesis of 1,4 di(S-sec propionic acid xanthate) butane (difunctional xanthate) RAFT agent (2)

Acetone (30 mL) was added to 1,4 butanediol (9.0 g, 0.1 mol) in a 250-mL round-bottomed flask. A solution of potassium hydroxide (11.2 g, 0.2 mol) in water (20 mL) was added to the reaction solution, which was then stirred for 2 hours. Carbon disulphide (15.2 g, 12 mL, 0.2 mol) was added dropwise to the mixture which had been cooled with an ice bath. The reaction was left stirring at low temperature for one hour. The formed yellow crystals were separated by filtration and washed with a solution of potassium chloride (25 g in 50 mL distilled water), to yield 15 g (47%) of dipotassium salt.

2-bromopropionic acid (3 g, 1.7 mL, 0.02 mol) was neutralized by a solution of potassium hydroxide (1.12 g, 0.02 mol) in distilled water (2 mL), and added to the dipotassium salt (3.2 g, 0.01 mol) in a 25-mL round-bottomed flask. The reaction mixture was stirred overnight and then acidified by the dropwise addition of 1 M hydrochloric acid. The reaction mixture was extracted with 40 mL ether, and the organic phase washed three times with 20 mL distilled water. The organic layer was dried over magnesium sulphate (anhydrous) and the solvent was evaporated. The residue was cooled in order to form crystals, and the product was recrystallized from 20 mL acetonitrile. A yellow crystalline product (1.3 g, 34% yield) was obtained, m.p. 100–102 °C.

^{1}H-NMR (DMSO): δ (ppm) = 1.46 (d, 3H, **CH_3**–, $J_{CH3–CH–} = 7.3$ Hz), 1.87 (p, 2H, –CH_2–**CH_2**–CH_2– $J_{CH2–CH2–CH2} = 2.7$ Hz), 4.31 (q, 1H, –**CH**–, $J_{CH3–CH–} = 7.3$ Hz), 4.61 (m, 2H, –**CH_2**–O–).

^{13}C-NMR (DMSO): δ (ppm) = 16.68 (**CH_3**–), 24.13 (CH_2–**CH_2**–CH_2–), 46.56 (–**CH–**), 73.81 (**CH_2**–O–), 172.21 (C=O), 212.33 (C=S).

FT-IR (photoacoustic cell) PAS (cm^{-1}) wavenumbers and their assignments: 3470 (–OH), 2970 (–CH_2–, –CH_3), 1712 (C=O), 1256 (C–O), 1072 (C=S), 884 (C–S).

UV(C=S): ($n \rightarrow \pi^*$, $\lambda_{max} = 356$ nm) and ($\pi \rightarrow \pi^*$, $\lambda = 281$). Acetonitrile was used as solvent.

Synthesis of 1,1,1 tri(S-sec ethyl propionate O-methylene xanthate) ethane (trifunctional) RAFT agent (3)

1,1,1-Tris(hydroxymethyl)ethane (2.4 g, 0.02 mol) was dissolved in DMSO (30 mL) at 60 °C. A solution of potassium hydroxide (5.04 g, 0.09 mol) in distilled water (10 mL) was added dropwise at room temperature. The reaction was cooled down in an ice bath and a large excess of carbon disulfide (60 g, 48 mL, 0.8 mol) was then slowly added over 20 minutes. The resulting dark red solution was stirred for two hours at room temperature. Then ethyl 2-bromo propionate (16.29 g, 11.6 mL, 0.09 mol) was slowly added over one hour at room temperature. The resulting yellow solution was stirred overnight. The reaction mixture was extracted with ether (250 mL) and the ether layer washed three times with 20 mL distilled water. The organic solution was then dried over magnesium sulphate (anhydrous), filtered and the solvent was evaporated under vacuum. The trifunctional xanthate RAFT agent **(3)** was finally purified by column chromatography on silica gel with hexane/ethyl acetate (7/3) mixture as eluent. A viscous yellow oil (6.8 g, 52% yield) was obtained.

^{1}H-NMR ($CDCl_3$): δ (ppm) = 1.21 (t, 9H, **CH_3**–CH_2–, $J_{CH3–CH2–} = 7.1$ Hz), 1.51 (d, 9H, **CH_3**–CH–, $J_{CH3–CH–} = 7.4$ Hz), 4.15 (q, 6H, CH_3–**CH_2**–, $J_{CH3–CH2–} = 7.1$ Hz), 4.33 (q, 3H, CH_3–**CH**–, $J_{CH3–CH–} = 7.4$ Hz), 4.54 (m, 6H, –C–**CH_2–**), 4.71 (m, 3H, –C–**CH_3**–).

^{13}C-NMR ($CDCl_3$): δ (PPM) = 13.79 (**CH_3**–CH_2–), 16.63 (**CH_3**–C–), 17.07 (**CH_3**–CH–), 39.68 (–**C**–), 49.39 (CH_3–**CH**–), 61.73 (CH_3–**CH_2**–), 74.45 (–C–**CH_2**–), 171.22 (C=O), 212.23 (C=S).

FT-IR (photoacoustic cell) PAS (cm^{-1}) wavenumbers and their assignments: 2977 ($-CH_2-$, $-CH_3$), 1735 (C=O), 1249 (C–O), 1049 (C=S), 864 (C–S).

UV(C=S): ($n \rightarrow \pi^*$, $\lambda_{max} = 431$ nm) and ($\pi \rightarrow \pi^*$, $\lambda = 280$ nm). Acetonitrile was used as solvent.

Synthesis of 1,1,1,1 tetra(S-sec ethyl propionate O-methylene xanthate) methane (tetrafunctional) RAFT agent (4)

The tetrafunctional xanthate RAFT agent was synthesized in the same way that was used for the trifunctional xanthate RAFT agent **(3)**. Reagents and quantities were as follows:

Pentaerythitol (0.02 mol, 2.72 g), DMSO (30 mL), potassium hydroxide (6.72 g, 0.12 mol), distilled water (10 mL), carbon disulfide (60.8 g, 48 mL), ethyl 2-bromo propionate (16.33 g, 11.7 mL, 0.09 mol), ether (250 mL).

The tetrafunctional xanthate RAFT agent **(4)** was purified by column chromatography on silica gel with a hexane/ethyl acetate (8/2) mixture as eluent. A very viscous yellow oil (10.7 g, 63% yield) was obtained.

^{1}H-NMR ($CDCl_3$): δ (ppm) = 1.14 (t, 12H, $\mathbf{CH_3}$–CH_2–, $J_{CH3-CH2-} = 7.1$ Hz), 1.43 (d, 12H, $\mathbf{CH_3}$–CH–, $J_{CH3-CH-} = 7.4$ Hz), 4.08 (q, 8H, CH_3–$\mathbf{CH_2}$–, $J_{CH3-CH2-} = 7.1$ Hz), 4.25 (q, 4H, CH_3–$\mathbf{CH}$–, $J_{CH3-CH-} = 7.4$ Hz), 4.66 (m, 8H, –C–$\mathbf{CH_2}$–).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 13.57 ($\mathbf{CH_3}$–CH_2–), 16.32 ($\mathbf{CH_3}$–CH–), 43.41 (–**C**–), 39.68 (–**C**–), 47.19 (CH_3–**CH**–), 61.48 (CH_3–$\mathbf{CH_2}$–), 70.46 (–C–$\mathbf{CH_2}$–), 170.74 (C=O), 211.5 (C=S).

FT-IR (photoacoustic cell) PAS (cm^{-1}) wavenumbers and their assignment: 2981 ($-CH_2-$, $-CH_3$), 1738 (C=O), 1242 (C–O), 1071 (C=S), 864 (C–S).

UV(C=S): ($n \rightarrow \pi^*$, $\lambda_{max} = 440$ nm) and ($\pi \rightarrow \pi^*$, $\lambda = 280$ nm). Acetonitrile was used as solvent.

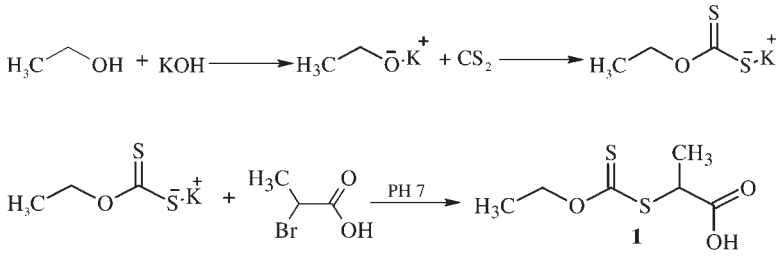
Synthesis of 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose-3-(S-sec ethyl propionoate) xanthate (monofunctional) RAFT agent (5)

Anhydrous acetone (500 mL) was added to a mixture of D (+) glucose (anhydrous, 75 g, 0.416 mol), zinc chloride (60 g) and 85% phosphoric acid (3.75 g). This mixture was stirred for 30 h at room temperature. The unreacted D-glucose (45 g) was collected on a filter and washed with a little anhydrous acetone. The filtrate was made alkaline (pH 10–11) with sodium hydroxide solution (42.5 g sodium hydroxide in 100 mL water). Precipitation of insoluble inorganic material occurred, which was removed by filtration. The colorless filtrate and washings were concentrated under reduced pressure. The residue was diluted with 75 mL water and extracted with chloroform (3×75 mL). The chloroform extracts were washed with a little water and then concentrated to yield a white crystalline residue, which was recrystallized from chloroform: hexane 1:2 to yield 27 g (41%) of crude 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose based on the reacted D (+) glucose anhydrous, m.p 107–110 °C.

^{1}H-NMR ($CDCl_3$): δ (ppm) = 1.3 (s, 3H, $\mathbf{CH_3}$), 1.35 (s, 3H, $\mathbf{CH_3}$), 1.43 (s, 3H, $\mathbf{CH_3}$), 1.48 (s, 3H, $\mathbf{CH_3}$), 2.74 (d, 1H, **OH**, $J_{H3-OH} = 2.8$ Hz), 3.98 (dd, 1H, $\mathbf{H_{6a}}$, $J_{H6a-H6b} = 8.7$ Hz, $J_{H6a-H5} = 5.3$ Hz), 4.05 (dd, 1H, $\mathbf{H_4}$, $J_{H4-H5} = 7.8$ Hz, $J_{H4-OH} = 2.8$ Hz), 4.15 (dd,1H, $\mathbf{H_{6b}}$, $J_{H6b-H6a} = 8.7$ Hz, $J_{H6b-H5} = 6.3$ Hz), 4.31 (m, 1H, $\mathbf{H_3}$), 4.32 (m, 1H, $\mathbf{H_5}$), 4.51 (d, 1H, $\mathbf{H_2}$, $J_{H2-H1-} = 3.6$ Hz), 5.92 (d, 1H, $\mathbf{H_1}$, $J_{H1-H2} = 3.6$ Hz).

An excess of sodium metal in the form of thin plates (1.2 g, 0.052 mol) was added in nine installments over 12 h, to a solution of (5 g, 0.019 mol) 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose in 20 ml dry ether. The reaction mixture was kept under reflux for 12 h, the ether solution was decanted and the residual sodium was washed with dry ether. The solution and the washings were combined and cooled in an ice bath. Carbon disulphide (10 mL) was added slowly and the mixture stirred at room temperature for 12 h resulting in a semi-solid, cream-colored mass of crude xanthate salt. Ethyl 2-bromo propionate (3.45 g, 2.4 mL, 0.019 mol) was slowly added to the crude xanthate salt at room temperature.

After being vigorously stirred at room temperature for 8 h, the reaction mixture



Scheme 1.
Preparation of S-sec propionic acid O-ethyl xanthate RAFT agent (1).

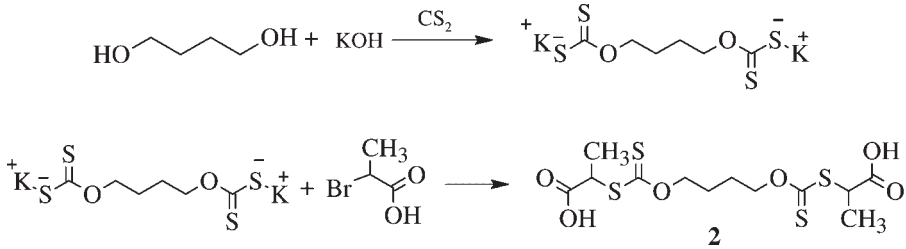
was extracted with 30 mL ether and, washed with 5 mL distilled water. The organic layer was dried over magnesium sulphate (anhydrous) and the solvent was evaporated. The xanthate RAFT agent **(5)** was finally purified by column chromatography on silica gel with a hexane/ethyl acetate (8/2) mixture as eluent. A viscous yellow oil (3 g, 36% yield) was obtained.

^{1}H-NMR ($CDCl_3$): δ (ppm) = 1.1 (t, 3H,CH_2–**CH_3**, $J_{CH2–CH3} = 6.9$ Hz), 1.3 (s, 3H, **CH_3**), 1.35 (s, 3H, **CH_3**), 1.43 (s, 3H, **CH_3**), 1.48 (s, 3H, **CH_3**), 1.5 (d, 3H, CH–**CH_3**, $J_{CH–CH3} = 7.8$Hz), 3.98 (dd, 1H, **H_{6a}**, $J_{H6a–H6b} = 8.7$Hz, $J_{H6a–H5} = 5.3$Hz), 3.9 (q, 2H, **CH_2**–CH_3, $J_{CH2–CH3} = 6.9$Hz), 4.01 (q, 1H, **CH**–CH_3, $J_{CH–CH3} = 7.8$Hz), 4.05 (dd, 1H, **H_4**, $J_{H4–H5} = 7.8$, $J_{H4–OH} =$ 2.8Hz), 4.15 (dd,1H, **H_{6b}**, $J_{H6b–H6a} = 8.7$Hz, $J_{H6b–H5} =$ 6.3Hz), 4.31(m, 1H, **H_3**), 4.32 (m, 1H, **H_5**), 4.51 (d, 1H, **H_2**, $J_{H2–H1–} =$ 3.6Hz), 5.92 (d, 1H, **H_1**, $J_{H1–H2} = 3.6$Hz).

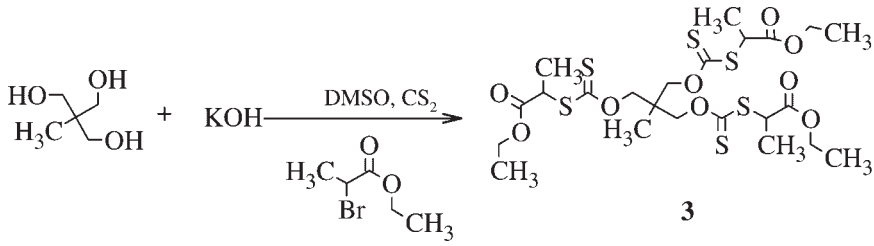
FT-IR (photoacoustic cell) PAS (cm^{-1}) wavenumbers and their assignments: 2986 (–CH_2–, –CH_3), 1737 (C=O), 1061 (C=S), 846 (C–S).

UV (C=S): ($n \rightarrow \pi^*$, $\lambda_{max} = 380$nm) and ($\pi \rightarrow \pi^*$, $\lambda = 280$ nm) Acetonitrile was used as solvent.

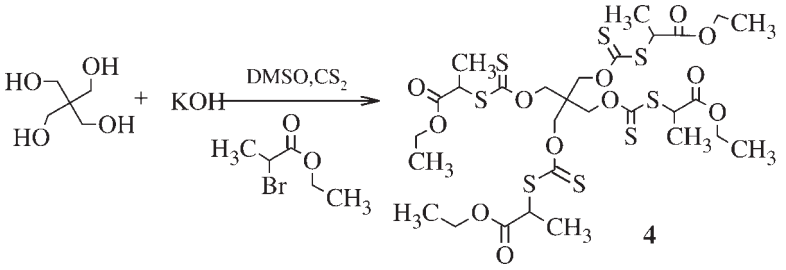
The chemical structures of the RAFT agents are given in Scheme 1–5.



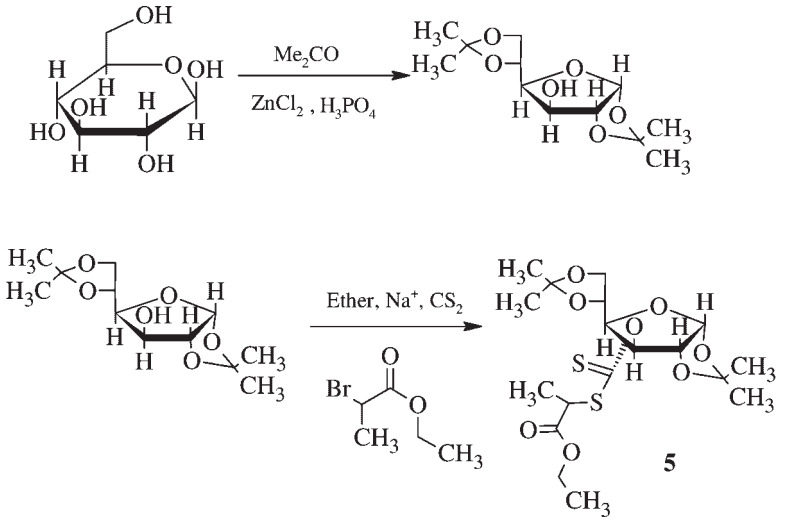
Scheme 2.
Preparation of 1,4 di(S-sec propionic acid xanthate) butane RAFT agent (2).



Scheme 3.
Preparation of 1,1,1 tri(S-sec ethyl propionoate O-methylene xanthate) ethane RAFT agent (3).



Scheme 4.
Preparation of 1,1,1,1 tetra(S-sec ethyl propionoate O-methylene xanthate) methane RAFT agent (4).



Scheme 5.
Preparation of 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose-3-(S-sec ethyl propionoate) xanthate RAFT agent (5).

Bulk Polymerization of Vinyl Acetate

Bulk polymerizations of vinyl acetate were performed in Schlenk tubes (to prevent evaporation of the highly volatile vinyl acetate) at 60 °C using 2,2 azobis(isobutyronitrile) (AIBN) as the initiator and xanthates **(1)**, **(2)**, **(3)**, **(4)**, **(5)** as RAFT agents. See Table 1 for experimental details.

The monomer, vinyl acetate, was first passed through a column of inhibitor remover packing, to remove the radical

Table 1.
The quantities of reagents used in bulk polymerization of vinyl acetate to produce linear and star shaped polyvinyl acetate. X indicates the monomer conversion.

Reaction	RAFT agent	RAFT (g)	AIBN (g)	Monomer (g)	X (%)	M_n,theory (g/mol)	M_n,SEC (g/mol)	M_n,MALLS (g/mol)	PDI
1	1	0.23	0.02	20	52	8 470	7 300	–	1.19
2	2	0.48	0.06	20	64	18 450	19 000	–	1.18
3	3	0.28	0.04	20	48	27 100	24 000	30 000	1.21
4	4	0.25	0.04	20	65	45 125	40 000	46 000	1.19
5	5	0.23	0.03	20	55	9 840	9 800	–	1.12

inhibitor, and then distilled under reduced pressure before utilization.

Before the polymerization reactions were started, the Schlenk tubes were deoxygenated by six consecutive freeze-pump-thaw cycles. All the reactions were conducted under nitrogen gas and samples were withdrawn at specific time intervals via a septum, until the reaction reached its final conversion. Conversions were calculated gravimetrically. The reactions were stopped by cooling in an ice bath. The polymer was isolated by evaporating the residual vinyl acetate initially in a fume hood, and then in a vacuum oven.

Results and Discussion

Here we present the use of five xanthate RAFT agents (monofunctional **(1)**, **(5)**, difunctional **(2)**, trifunctional **(3)** and tetrafunctional **(4)** xanthate RAFT agents) in bulk polymerizations to produce living polyvinyl acetate homopolymer. Table 1 describes the experimental conditions for the homopolymerizations of vinyl acetate.

It should be noted that difunctional xanthate RAFT agent **(2)** is symmetrical and has the ability to fragment on two sides, while xanthate RAFT agents **(1)** and **(5)** are monofunctional and can fragment only in one place. On the other hand xanthate RAFT agents **(3)** and **(4)** are trifunctional and tetrafunctional and they can fragment on three and four sides respectively, growth therefore takes place in both sides of the difunctional xanthate RAFT agent **(2)** while takes place in three and four sides of the trifunctional **(3)** and tetrafunctional **(4)** respectively.

Figure 1 shows the logarithm of normalized monomer concentration versus time for reactions (1) to (5). The linearity of the curves indicates that there is a steady-state radical concentration, which means that the rate of radical generation and the rate of radical loss are equivalent during the course of the reactions, while the initiator concentration is sufficient in the system. In other words the number of growing chains (propagating species) is constant throughout the polymerization reactions.

Prominent inhibition periods were observed for reactions (3) and (4), where trifunctional **(3)** and tetrafunctional **(4)** xanthate RAFT agents were used for the preparation of star shaped polymers. The inhibition periods were barely observed for reactions (1), (2) and and (5), where

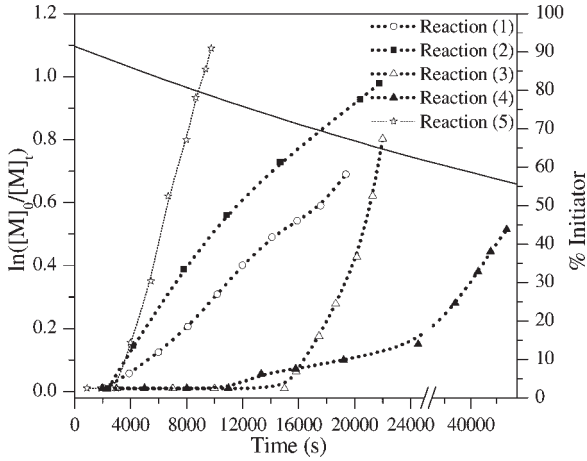


Figure 1.
Semilogarithmic plots of fractional conversion versus time for vinyl acetate mediated homopolymerizations by xanthate RAFT agents (1), (2), (3) (4) and (5) (reactions 1, 2, 3, 4 and 5). Dotted lines have been added as guides for the eye. See Table 1 for experimental details.

monofunctionals and difunctional xanthate RAFT agents were used to prepare the linear shaped polymer.

The most likely reason for these inhibition periods is that, as proposed by Bernard,[26] trace levels of impurities, too low to be detected on thin-layer chromatography plates are responsible.

The evaluation of experimental molar masses and molar mass distributions with conversion was investigated by SEC analysis for reactions (1) to (5) (see also Figure 2 as an example). Each chromatogram exhibited a narrow monomodal molar mass distribution, and the molar mass increased with conversion, indicating the successful living polymerization of vinyl acetate.[27]

Figure 3 shows that $\overline{M}_n$ increases linearly as a function of monomer conversion. This is an indication there were a constant number of growing chains during the polymerizations which means there was control over molar mass during the reaction.[28] The experimental and theoretical $\overline{M}_n$ values are similar for all the reactions from (1) to (5).

The theoretical number average molar masses were calculated using the following equation:[5]

$$\overline{M}_{n,theory} = \frac{x[M]_0}{[RAFT]_0} M_M + M_{RAFT} \quad (1)$$

where $[M]_0$ and $[RAFT]_0$ are the initial concentrations of the monomer and the RAFT agent, M_M and M_{RAFT} are the molar masses of the monomer and the RAFT agent respectively, x is the fractional conversion and $\overline{M}_{n,theory}$ is the theoretical number average molar mass of the formed polymer.

The lower values of experimental $\overline{M}_n$ observed in reactions (3) and (4) (see Figure 3) could be due to the fact that, as the star polymers have lower hydrodynamic volumes than the equivalent linear polymers,[26,29] the experimental molar mass of the star polymer observed in reactions (3) and (4) determined by SEC with linear PS standards appeared slightly lower than the theoretical $\overline{M}_n$ as can be seen in Figure 3.

The reduced accessibility of the thio carbonyl thio moiety at higher polymer conversion contributed to this deviation. The thio carbonyl thio moiety is localized close the core and is shielded by an increasing PVAc layer.[20,29] The propagating radical is not able to reach the RAFT

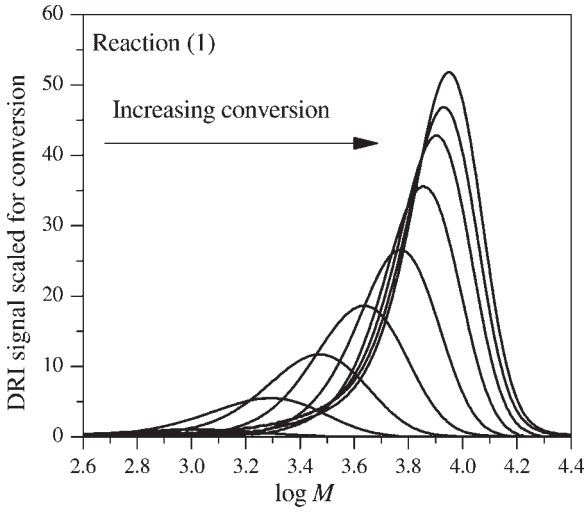


Figure 2.
Molar mass distribution of samples scaled for conversion taken from reactions (1) where RAFT (1) was used, .All reactions conditions are listed in Table 1.

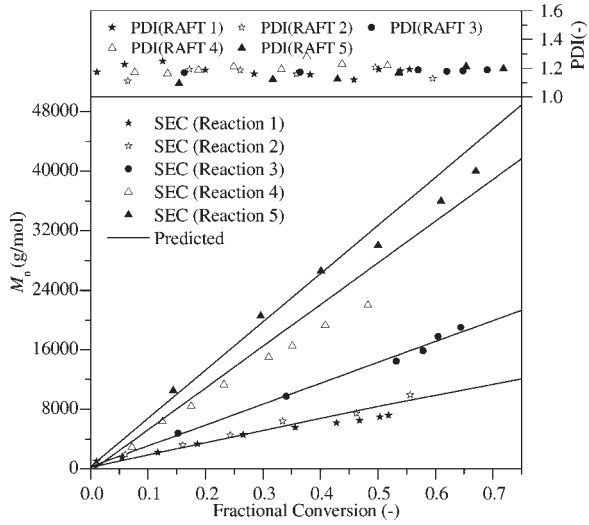


Figure 3.
Evolution of $\overline{M}_n$ and polydispersity as a function of conversion, for RAFT mediated polymerization of vinyl acetate prepared from reactions (1) to (5). Refer to Table 1 for reactions conditions.

group and therefore preferentially terminates.[30]

To determine deviations from the linear, calibration using a multi-angle laser light scattering detector (MALLS) was used to determine the absolute molar mass for the star polymers. The molar masses of the star polymers obtained by MALLS ($\overline{M}_n$ 3arms = 30,000 g/mol, $\overline{M}_n$ 4arms = 46,000 g/mol), were higher than the molar masses obtained by SEC ($\overline{M}_n$ 3arms = 24,000 g/mol, $\overline{M}_n$ 4arms = 40,000 g/mol).

The obtained polydispersities of the generated polyvinyl acetates are close to or below 1.3 throughout the reactions, as can be seen from inspection of Figure 3. This is a characteristic of living radical polymerization.

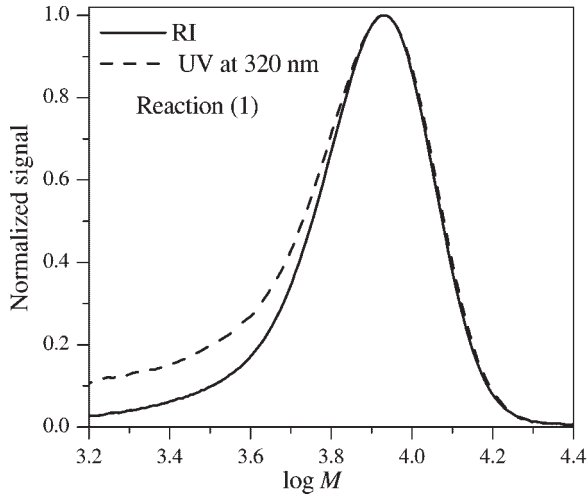


Figure 4.
UV-RI overlays for RAFT mediated polymerization of vinyl acetate prepared from reaction (1) where RAFT (1), were used. All reactions conditions are listed in Table 1.

The presence of thio carbonyl thio moeities can be examined using dual detectors for SEC. UV and RI detectors were used to determine whether the polymer chains have the thio carbonyl thio moeity. The UV detector was set at 320 nm as the thio carbonyl bond (C=S) of xanthate RAFT agent absorbs strongly at this wavelength,[31] and the RI is a concentration sensitive detector.

Figure 4 shows an example of the overlay comparisons of the two signals which can indicate whether the RAFT functionality is homogenously or heterogeneously distributed throughout the molar mass distribution curve.

One of the factors affecting the UV signal is the dilution effect due to an increase in molecular weight, which results in a weaker signal at high molecular weight. At low molar mass the UV signal observed is very strong due to the fact that the chains are small, resulting in a high concentration of RAFT agent per mass of chain. The Figure 4 shows that the RAFT moiety was homogenously distributed, as indicated by the UV-RI overlays.

Conclusions

The chain transfer ability of the five synthesized xanthate (MADIX)/RAFT agents to induce living characteristics in free radical polymerization of vinyl acetate was investigated with respect to molar mass control and kinetic behavior. These five compounds, S-sec propionic acid O-ethyl xanthate RAFT agent **(1)**, 1,4 di(S-sec propionic acid xanthate) butane RAFT agent **(2)**, 1,1,1 tri(S-sec ethyl propionoate O-methylene xanthate) ethane RAFT agent **(3)**, 1,1,1,1 tetra(S-sec ethyl propionoate O-methylene xanthate) methane RAFT agent **(4)** and 1,2:5,6-Di-O-isopropylidene - α-D-glucofuranose -3 -(S-sec ethyl propionoate) xanthate RAFT agent **(5)** were identified as suitable xanthate (RAFT MADIX) agents, yielding linear and star shaped polyvinyl acetate with low polydispersities and molar masses ranging from 1,000 to 40,000 g/mol.

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