**MADIX Polymerization of Vinyl Acetate using Ethyl Acetate as a Green Solvent; Near Complete Monomer Conversion with Molecular Weight Control**

**Supplementary Information**

Martin E. Levere, Pierre Chambon, Steve P. Rannard and Tom O. McDonald

Department of Chemistry, University of Liverpool, Crown Street, L69 7ZD, United Kingdom

Correspondence to: Tom McDonald (E-mail: [*Thomas.mcdonald@liverpool.ac.uk*](mailto:Thomas.mcdonald@liverpool.ac.uk))

**1. Materials and Characterisation**

**1.1 Instrumentation**

1H nuclear magnetic resonance (NMR) spectra were recorded in Chloroform-d3 (conversion analysis) or Methanol-d3 (for product analysis) using a Bruker Avance spectrometer operating at 400 MHz and calibrated against tetramethylsilane as an internal standard. Triple detection gel permeation chromatography size exclusion chromatography was performed using a Malvern Viscotek instrument equipped with a GPCmax VE2001 auto-sampler, two Viscotek T6000 columns (and a guard column), a refractive index (RI) detector VE3580 and a 270 Dual Detector (light scattering and viscometer) with a mobile phase of THF containing 2 v/v% of triethylamine and a flow-rate of 1 mL min-1. All polymerization reactions were performed in 15 mL ACE Glass pressure tubes (Manufacturer Number 8648-164) with Teflon screw cap and fitted with a plunger valve and thermowell and with an internal O-ring seal.

**1.2 Materials**

Vinyl acetate (99%) was purchased from Aldrich passed through a column of basic alumina before use to remove the inhibitor. Azobisisobutyronitrile (AIBN) (97%) and Azobis(4-cyanovaleric acid) (ACVA) were purchased from Aldrich were stored at 4°C and used as received within 3 months of receipt. Dichloromethane (DCM) (Laboratory Reagent Grade) and ethyl acetate (EtAc) (Analytical Reagent Grade) were purchased from Fisher and used as received. Potassium Ethyl Xanthate (98%) was purchased from Alfa Aesar and used as received. Benzyl bromide (98%) was purchased from Fluka and used as received. Acetone (Analytical Reagent Grade) was obtained from Fisher and used as received.

**2. Experimental Procedures**

**2.1 Synthesis of MADIX Agent S-benzyl-O-ethyl dithiocarbonate**

Potassium ethyl xanthate (2.80g, 0.021 mol.) was charged to a round bottomed flask along with a Teflon coated magnetic stirring bar and dissolved in approximately 20 mL acetone. Separately, benzyl bromide (3.10 g, 0.0175 mol.) was dissolved in 20 mL of acetone and added dropwise to the potassium ethyl xanthate (see scheme 1). The reaction mixture changed colour from yellow to white. After 2h stirring the mixture was filtered to remove the white salt and the product extracted using a DCM / brine separating funnel. The organic layer was collected, re-filtered and dried under vacuum to give a yellow oil. Typical Yield = 2.97 g, Purity > 97% (NMR).

  
**Scheme S1:** Synthesis of MADIX Agent S-benzyl-O-ethyl dithiocarbonate.

**Analysis**

1H NMR (400 MHz, CDCl3, δ): 7.49 (m, 5H, Ar H), 4.64 (q, 2H; CH2-O), 4.30 (s, 2H; S-CH2) 1.41 (t, 3H; CH3). Spectrum is shown in figure S1.



**Figure S1:** 1H NMR Spectrum of MADIX Agent S-benzyl-O-ethyl dithiocarbonate

**2.2 Polymerisations of Vinyl Acetate**

**Typical Procedure for polymerisation of Vinyl Acetate**

Polymerisation of vinyl acetate was performed in ACE Glass pressure tubes at ratio ranging from [M]0/[CTA]0/[AIBN]0 = 25/1/0.2 to 3000/1/0.2. Vinyl acetate (2.0 g, 0.232 mol.) was charged to an ACE Glass pressure tube fitted with plunger valve, thermowell and back seal along with a Teflon coated stirring bar, MADIX agent S-benzyl-O-ethyl dithiocarbonate and initiator AIBN and solvent (2.0 mL, or 0 mL in bulk) and the mixture deoxygenated by a series of freeze pump thaw cycles from liquid nitrogen using standard Schlenk techniques. Polymerisations were typically performed under vacuum, however some were performed under nitrogen. It was found that removing the thermowell from the plunger valve facilitated freeze-pump thawing. The reaction mixture was placed in a thermostatted oil bath operating at 70°C to react for a fixed time of 48h. No increase in viscosity was observed for periods up to 24h, however polymer had formed after 48h in accordance with a previously observed induction period. After 48h a sample was taken to measure conversion by 1H NMR analysis and the polymer product precipitated into cold petroleum ether, collected and dried for 24h under vacuum.

On a practical point of view, 70 °C is about 3 °C below the boiling point of vinyl acetate and 7 °C below the boiling point of ethyl acetate and was selected to limit the possible pressure build up in the reactor. However, in order to minimise the risks, pressure reactor were used throughout the series of experiments. Note that for the synthesis carried out in DCM, the person carrying out the experiment MUST use a pressure tube as the boiling point of DCM is about 39 °C.

Representative characterisation data for PVAc with [M]0/[CTA]0 = 100: 1H NMR (400 MHz, CDCl3): δ = 4.89 (br, 1H; –CHO–CH2), δ = 2.01 (br, 3H; –CO–CH3), δ = 1.85 (br, 2H; –CH2–). Representative spectrum for PVAc polymerized in DCM is shown in figure S2.

****

**Figure S2:** 1H NMR spectrum (400 MHz, CDCl3) of poly(vinyl acetate) prepared in dichloromethane mediated by S-benzyl-O-ethyl dithiocarbonate using ratio [M]0/[CTA]0 = 100



**Figure S3:** MADIX polymerisation of vinyl acetate mediated by S-benzyl-O-ethyl dithiocarbonate in ACE Glass pressure tubes at 70oC in bulk. (A) Plot of experimentally measured (GPC with Triple Detection) number average molecular weight (*Mn*) and *Mw/Mn* versus theoretical molecular weight (*Mn)*. The line represents the theoretical value. Conditions: Vinyl acetate = 2.0 g, Solvent = 0 mL. Fixed Ratio [CTA]0 / [AIBN]0 = 1/0.2. (B-F) Raw SEC chromatograms in THF from the RI detector are shown, corresponding to a different [M]0/[CTA]0.



**Figure S4:** MADIX polymerisation of vinyl acetate mediated by S-benzyl-O-ethyl dithiocarbonate in ACE Glass pressure tubes at 70oC in DCM. (A) Plot of experimentally measured (GPC with Triple Detection) number average molecular weight (*Mn*) and *Mw/Mn* versus theoretical molecular weight (*Mn)*. The line represents the theoretical value. Conditions: Vinyl acetate = 2.0 g, Solvent = 2 mL. Fixed Ratio [CTA]0 / [AIBN]0 = 1/0.2. (B-F) Raw SEC chromatograms in THF from the RI detector are shown, corresponding to a different [M]0/[CTA]0.



**Figure S5:** MADIX polymerisation of vinyl acetate mediated by S-benzyl-O-ethyl dithiocarbonate in ACE Glass pressure tubes at 70oC in ethyl acetate. (A) Plot of experimentally measured (GPC with Triple Detection) number average molecular weight (*Mn*) and *Mw/Mn* versus theoretical molecular weight (*Mn)*. The line represents the theoretical value. Conditions: Vinyl acetate = 2.0 g, Solvent = 2 mL. Fixed Ratio [CTA]0 / [AIBN]0 = 1/0.2. (B-F) Raw SEC chromatograms in THF from the RI detector are shown, corresponding to a different [M]0/[CTA]0.



**Figure S6:** Overlaid GPC traces from the RI detector for polymerization of vinyl acetate in the presence or absence of chain transfer agent. The samples were prepared by MADIX polymerization of vinyl acetate in ethyl acetate mediated by S-benzyl-O-ethyl dithiocarbonate in ACE Glass pressure tubes at 70 °C for 48h and initiated by AIBN. Conditions Vinyl Acetate = 2.0 g, ethyl acetate = 2 mL, [CTA]0/[AIBN]0 = 1/0.2.

**2.3 Chain Extension Procedures**

The molecular weight of the starting macro chain transfer agents is approx. 7680 g mol-1 from ethyl acetate as the products of the MADIX polymerisations at ratio [M]0/[CTA]0/[AIBN]0 = 100/1. Vinyl acetate (1 mL) was charged to an ACE Glass pressure tube with a stirring bar along with macroCTA (0.25 g) and AIBN (0.0015 g) and solvent ethyl acetate (1 mL, used for both chain extensions). The tube was deoxygenated through the plunger valve by a series of freeze pump thaw cycles from liquid nitrogen and sealed under an atmosphere of nitrogen. The pressure tube was placed in a thermostatted oil bath operating at 70°C for 24h. After this time had elapsed the mixture in the tube had become viscous. The product was precipitated into cold petroleum ether and analysed by SEC in THF with respect to the macro chain transfer agent starting material. To achieve a greater separation by SEC for the macroCTA and chain extended block copolymer, 4 mL of vinyl acetate and 4 mL of ethyl acetate were used in the reaction mixture, along with 0.25g macroCTA and 0.0010 g of AIBN.



**Figure S7:** Overlaid SEC Chromatograms for the chain extension of poly(vinyl acetate) macro chain transfer agent (MacroCTA) prepared ethyl acetate with vinyl acetate in ACE Glass pressure tubes at 70°C in ethyl acetate (EtAc) solvent. (A) Vinyl acetate = 1 mL, MacroCTA = 0.5 g, Solvent = 1 mL (B) Vinyl acetate = 4 mL, MacroCTA = 0.25 g, Solvent = 4 mL (b,d). Fixed Ratio [MacroCTA]0 / [AIBN]0 = 1/0.2 in all polymerizations. Raw SEC chromatograms in THF from the refractometer are shown, corresponding to each data point.