ELECTRONIC SUPPORTING INFORMATION

Nitroxide Mediated Polymerisation of Thioacrylates and Their Transformation into Poly(acrylamide)s

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1. Experimental

1.1 Instrumentation

1.1.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry was performed by use of a Model DSC 25 Differential Scanning Calorimeter (TA Instruments) under N₂ atmosphere (50 mL/min). An indium standard \(T_m = 156.6 \, ^\circ C \) and \( \Delta H = 28.72 \, \text{J/g} \) was used to calibrate the instrument according to the manufacturer instructions. Preweighed (3−8 mg) finely powdered samples were taken in a standard sealed 50 µL hermetic aluminum pan for the measurement. Instrument was equilibrated at 25 °C and then heated to 180 °C at a rate of 10 °C/min, holding for 1 minute, and then cooling back to −80 °C. DSC was then conducted while heating to 180 °C at 10 °C/min. The cooling and
heating scans were repeated twice to erase the effect of previous thermal history of the samples. Data were collected with TA software (version V4.3.1.39215) where from the DSC curves $T_g$ were determined from the inflection point temperature and from the heat flow derivative (DDSC) curve.

1.1.2 Gel permeation chromatography (GPC)

GPC was utilised to determine molecular weight averages and polymer dispersity. GPC measurements were performed on an Agilent 390-LC system equipped with a PL-AS RT autosampler, 2PLgel 5 µm mixed-C columns (300×7.5 mm), a PLgel 5 mm guard column (50×7.5 mm), and a differential refractive index (DRI). The system was eluted with THF containing 2% trimethylamine (TEA) at a flow rate of 1 mL min$^{-1}$ and the DRI was calibrated with linear narrow poly(methyl methacrylate) standards ranging from 1010 to 21360000 g/mol, purchased from Agilent Technologies (UK).

1.1.3 Nuclear magnetic resonance (NMR)

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AV-400 at 303 K. CDCl$_3$ and the resonance signal at 7.26 ppm ($^1$H) was used as residual CDCl$_3$ or for (CD$_3$)$_2$CO at 2.05 ppm peak for the chemical shift ($\delta$).

Monomer conversions for kinetic investigation were calculated via $^1$H NMR comparing the ratios of the vinyl signals of monomers (between 6.50 and 5.50 ppm) and their corresponding methyl signals in the side chain (between 1.00 and 0.80 ppm). The conversion for PFS was calculated via $^1$H NMR comparing the ratios of the vinyl signals (between 6.50 and 5.50 ppm) from samples taken at predetermined times with a $t_0$ sample taken prior polymerization.

1.2 Materials

All chemicals and solvents were commercially available and used as received unless otherwise stated. 1-Butanethiol (Aldrich, 99%), 14-(Dimethylamino)pyridine (DMAP, Aldrich, 99%), Bromoacetic acid (Aldrich, reagent grade, 97%), Butanethiol Aldrich, 99%), Dicyclohexylcarbodiimide (DCC, Aldrich, puriss., $\geq$99% (GC)), Ethanethiol (Sigma, 97%), Paraformaldehyde (Sigma, powder, 95%), Potassium carbonate
(Sigma, BioXtra, ≥99%), Thiophenol (Sigma, 97%) and Triethylamine (TEA, Sigma, ≥99%). All solvents were purchased from Sigma-Aldrich (UK) and used as received at the highest purity available. SG1-MAMA was kindly provided from Arkema and used as received.

1.3 Procedures

1.3.1 Synthesis of Ethyl thioacrylate (ETA) and Butyl thioacrylate (BuTA)

ETA was synthesized according to the literature and the obtained analytical data were in accordance with the literature\textsuperscript{1}. BuTA was synthesized according to the literature procedure.

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \(\delta = 6.40 \text{ (dd, 1H, J = 9.8 Hz, H\textsubscript{a1})}, 6.29 \text{ (dd, 1H, J = 12.2 Hz, H\textsubscript{b})}, 5.66 \text{ (dd, 1H, J = 9.9 Hz)}, 2.97 \text{ (t, J = 7.3 Hz, 2H, J = 7.3 Hz, H\textsubscript{c})}, 1.6 \text{ (quin, 2H, J = 7.4 Hz, H\textsubscript{d})}, 1.42 \text{ (sex, 2H, J = 7.4 Hz, H\textsubscript{e})} \text{ and 0.94 (t, 3H, J = 7.3 Hz, H\textsubscript{f})}.

![Figure S1: \textsuperscript{1}H-NMR spectrum (CDCl\textsubscript{3}, 400 MHz, 303 K) of BuTA](image-url)
1.3.2 Synthesis of Poly(butyl thioacrylate) (P1)

To a flame-dried Schlenk flask, equipped with a magnetic stir bar and under N$_2$-atmosphere, SG1-MAMA (15.6 mg, 0.04 mmol), butylacrylate (300 mg, 2.08 mmol) and 1.06 mL dry DMF was added. The reaction mixture was degassed by gentle bubbling of N$_2$ gas for 30 minutes at room temperature. The Schlenk tube was submerged into the pre-heated oil bath at 70 °C to start the polymerisation. Samples were taken via degassed syringe at desired time points and analysed. The samples were then analysed by GPC and $^1$H NMR.

Table S1: Data obtained from the homopolymer of BuTA, at 70 °C in DMF (P1).

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$M_{n,\text{theo}}$ (g/mol)</th>
<th>$M_{n,\text{GPC}}$[b] (g/mol)</th>
<th>PDI[b]</th>
<th>Conv.[a] (%)</th>
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Polymerisation condition: ([M]$_0$:[SG1-MAMA]$_0$ = 50:1) in DMF at 70 °C for BuTA for P1. [a] Conversion measured by $^1$H NMR spectroscopy. [b] THF eluent, linear PMMA standard.
1.3.3. Synthesis of Poly(butyl acrylate) (P2)

To a flame-dried Schlenk flask, equipped with a magnetic stir bar and under N₂-atmosphere, SG1-MAMA (31.4 mg, 0.08 mmol), butylacrylate (532 mg, 4.15 mmol) and 1.06 mL dry DMF was added. The reaction mixture was degassed by gentle bubbling of N₂ gas for 30 minutes at room temperature. The Schlenk tube was submerged into the pre-heated oil bath at 70 °C to start the polymerisation. Samples were taken via degassed syringe at desired time points and analysed. The samples were then analysed by GPC and ¹H NMR.

Table S2: Data obtained from the homopolymer of BuA, at 70 °C in DMF (P1).

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$M_{n,\text{theo}}$ (g/mol)</th>
<th>$M_{n,\text{GPC}}$[b] (g/mol)</th>
<th>PDI[b]</th>
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<td>1200</td>
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1.3.4. Synthesis of Poly(butyl thioacrylate) (P3)

To a flame-dried Schlenk flask, equipped with a magnetic stir bar and under N₂-atmosphere, SG1-MAMA (15.9 mg, 0.04 mmol), butyl thioacrylate (300 mg, 2.08 mmol) and 0.60 mL dry DMF was added. The reaction mixture was degassed by gentle bubbling of N₂ gas for 30 minutes at room temperature. The Schlenk tube was submerged into the pre-heated oil bath at 120 °C to start the polymerisation. Samples were taken via degassed syringe at desired time points and analysed. The samples were then analysed by GPC and ¹H NMR.

<table>
<thead>
<tr>
<th>Time (min)</th>
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<th>Mₙ,GPC (g/mol)</th>
<th>PDI</th>
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Table S3: Data obtained from the homopolymer of BuTA, at 120 °C in DMF (P3).

Figure S4: GPC traces of the homopolymerisation at 120 °C in DMF. For BuTA with DP = 50 (P3)
1.3.5. Synthesis of Poly(butyl acrylate) (P4)

To a flame-dried Schlenk flask, equipped with a magnetic stir bar and under N₂-atmosphere, SG1-MAMA (31.6 mg, 0.08 mmol), butylacrylate (533 mg, 4.16 mmol) and 1.06 mL dry DMF was added. The reaction mixture was degassed by gentle bubbling of N₂ gas for 30 minutes at room temperature. The Schlenk tube was submerged into the pre-heated oil bath at 120 °C to start the polymerisation. Samples were taken via degassed syringe at desired time points and analysed. The samples were then analysed by GPC and ¹H NMR.

Table S4: Data obtained from the homopolymer of BuTA, at 120 °C in DMF (P4).

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$M_n\text{,theo}$ (g/mol)</th>
<th>$M_n\text{,GPC}$[b] (g/mol)</th>
<th>PDI[b]</th>
<th>Conv.[a] (%)</th>
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Polymerisation condition: ([M][0]:[SG1-MAMA][0] = 50:1) in DMF at 120 °C for BuA for . [a] Conversion measured by ¹H NMR spectroscopy. [b] THF eluent, linear PMMA standard.

Figure S5: GPC traces of the homopolymerisation at 120 °C in DMF. For BuA with DP = 50 (P4).
1.3.6. Synthesis of copolymer of BuTA with PFS (P5)

To a flame-dried Schlenk flask, equipped with a magnetic stir bar and under \( \text{N}_2 \)-atmosphere, SG1-MAMA (69.8 mg, 0.18 mmol), butyl thioacrylate (659 mg, 4.58 mmol), PFS (887 mg, 4.57 mmol) and 3.10 mL dry DMF was added. The reaction mixture was degassed by gentle bubbling of \( \text{N}_2 \) gas for 30 minutes at room temperature. The Schlenk tube was submerged into the pre-heated oil bath at 120 °C to start the polymerisation. Samples were taken via degassed syringe at desired time points and analysed. The samples were then analysed by GPC and \(^1\)H NMR.

![Figure S6: GPC traces of the copolymerisation of PFS with BuA (P5, black trace) and PFS with BuTA (P6, red trace) with DP = 50 in DMF at 120 °C.](image)

1.3.7. Synthesis of copolymer of BuA with PFS (P6)

To a flame-dried Schlenk flask, equipped with a magnetic stir bar and under \( \text{N}_2 \)-atmosphere, SG1-MAMA (69.4 mg, 0.18 mmol), butylacrylate (585 mg, 4.58 mmol), PFS (887 mg, 4.57 mmol) and 3.00 mL dry DMF was added. The reaction mixture was degassed by gentle bubbling of \( \text{N}_2 \) gas for 30 minutes at room temperature. The Schlenk tube was submerged into the pre-heated oil bath at 120 °C to start the polymerisation. Samples were taken via degassed syringe at desired time points and analysed. The samples were then analysed by GPC and \(^1\)H NMR.
1.3.8. Synthesis of Poly(ethyl thioacrylate) (P7)

To a flame-dried Schlenk flask, equipped with a magnetic stir bar and under N\textsubscript{2}-atmosphere, SG1-MAMA (1.00 g, 2.62 mmol), ethyl thioacrylate (6.10 g, 52.5 mmol) and 12 mL dry DMF was added. The reaction mixture was degassed by gentle bubbling of N\textsubscript{2} gas for 30 minutes at room temperature. The Schlenk tube was submerged into the pre-heated oil bath at 120 °C to start the polymerisation. Samples were taken via degassed syringe at desired time points and analysed. The samples were then analysed by GPC, GC and \textsuperscript{1}H NMR. The reaction was stopped by immersion of the reaction flask into liquid N\textsubscript{2}. After 1.5h \textsuperscript{1}H NMR showed full conversion, DMF was distilled of and the polymer was dried until constant weight to yield P(ETA) as a yellow sticky compound (4.00 g, 56% yield). \( M_n,\text{theo} = 2700 \text{ g/mol}, M_n,\text{GPC} = 1290 \text{ g/mol}, \text{PDI} = 1.24. \)

**Scheme S1:** Schematic representation of the overall reaction scheme for the preparation of homopolymer P7.
Figure S7: $^1$H NMR spectra displaying full monomer consumption for homopolymerisation of ethyl thioacrylate (CDCl$_3$, 400 MHz, 303 K).

Figure S8: $^1$H NMR spectra of purified poly(ethyl thioacrylate) (CD$_3$)$_2$CO, 400 MHz, 303 K).
Figure S9: $^{13}$C NMR spectrum of P(ETA) (DP=20) in CDCl$_3$ by NMP at 120 °C. The numbering of the carbon atoms used for the NMR peak assignment is shown in the spectrum.

Figure S10: GPC trace of the obtained poly(ethyl thioacrylate)s with DP = 20 in DMF at 120°C via NMP.
1.3.9. General procedure for microwave assisted functionalisation (P8-P16)

Microwave syntheses were performed using a Biotage microwave synthesiser (Biotage® Initiator+) using a 4 mL borosilicate sealable microwave tube. P7 was weighed into the microwave tube. THF was added, a magnetic stirrer bar added and TEA and PhSH was subsequently added. The vessel was sealed and the reaction mixture was sonicated briefly and then heated under microwave irradiation for a predetermined time. After the reaction was finished, the reaction vessel was allowed to cool down and diluting in THF. The work-up procedure consisted of dialysing against 2 x 3 L THF/H₂O (9:1). THF was evaporated and the resulting mixture was freeze dried to give the pure polymers.

Figure S11: ¹H NMR analysis of the reaction between the thioester containing polymer P7 and benzylamine in the presence of thiophenol forming thioester-amide containing polymer P8.
Figure S12: GPC traces (RID) of P(ETA) before (P7) and after nucleophilic substitution with benzylamine (P8).

Figure S13: a) Visual appearance of Poly(ethyl thioacrylate) P7. b) Appearance of the post-polymerisation modified polymers with 22% of BzAm in the final copolymer P8.
Figure S14: $^1$H NMR analysis of the reaction between the thioester containing polymer P7 and benzylamine in the presence of thiophenol forming thioester-amide containing polymer P9.

Figure S15: $^1$H NMR analysis of the reaction between the thioester containing polymer P7 and benzylamine in the presence of thiophenol forming thioester-amide containing polymer P10.
Figure S16: $^1$H NMR analysis of the reaction between the thioester containing polymer P7 (bottom) and benzylamine in the presence of thiophenol forming thioester-amide containing polymer P11 (top).

Figure S17: GPC traces (RID) of P(ETA) before (P7) and after nucleophilic substitution with benzylamine (P11).
1.3.11. General procedure for microwave assisted functionalisation with isopropylamine (P17)

In a vial, 156 mg of the purified polymer was dissolved in 1.20 mL of dry THF. Ten equivalents of isopropylamine was added to the mixture followed by two equivalents of TEA and two equivalents of thiophenol (in respect of a polymer single unit) and stirred overnight at 75 °C in the microwave for 48h. The mixture was then dialysed against THF/H₂O (9:1), evaporated and freeze dried to give the corresponding polymer.

**Figure S18:** Obtained GPC traces of P17 and P7.

![Normalized RI Signal vs Retention Time](image)

**Figure S19:** Visual appearance of Poly(ethyl thioacrylate) P7. b) Appearance of the post-modified polymer P17.
1.3.12. General procedure for microwave assisted functionalisation with benzylalcohol (P18)

In a vial, 80.0 mg of the purified polymer was dissolved in 0.60 mL of dry THF. Ten equivalents of benzylalcohol (0.24 mL, 2.20 mg) was added to the mixture followed by two equivalents of TEA and two equivalents of thiophenol (in respect of a polymer single unit) and stirred overnight at 75 °C in the microwave for 48h. The mixture was then dialysed against THF/H₂O (9:1), evaporated and freeze dried to give the corresponding polymer.

1.3.13. Synthesis of Poly(benzyl acrylamide) (P19)

In a typical polymerisation, to benzyl acrylamide (0.32 g, 1.99 mmol) was added V-601 (2.28 mg, 9.90 μmol), dioxane (0.3 mL) and BDTMP (41.6 mg, 98.9 μmol). The constituents were mixed together with a vortex mixer and charged into a Schlenk tube, sealed with a rubber septum and degassed by gentle bubbling of N₂ gas for 30 minutes. The Schlenk tube was then immersed into an oil bath at 100 °C. Samples were taken via degassed syringe at desired time points and analysed. Dioxane was distilled of and the polymer was dried until constant weight to yield a white compound. \( M_n,\text{theo} = 3640 \text{ g/mol} \), \( M_n,\text{GPC} = 3300 \text{ g/mol} \), PDI = 1.27. The samples were then analysed by GPC, DSC and \(^1\text{H}\) NMR.

![Figure S20: GPC trace of the obtained poly(benzylacrylamide) with DP = 20 in dioxane at 100 °C via RAFT.](image-url)
2. Characterisation of compounds

**Figure S21**: P7 DSC Thermogram

**Figure S22**: P12 DSC Thermogram
Figure S23: P13 DSC Thermogram

Figure S24: P14 DSC Thermogram
Figure S25: P15 DSC Thermogram

Figure S26: P16 DSC Thermogram
Figure S27: P18 DSC Thermogram

3. References