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Copper mediated RDRP of thioacrylates and their combination with acrylates and acrylamides†

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Thioacrylates are a novel class of monomers that have been shown to be polymerisable. However, knowledge of their polymerisation behaviour in metal mediated radical polymerisation is limited, although the thioester functionality allows efficient post modifications. In this report, findings on the polymerisation of thioacrylates *via* SET-LRP conditions are presented. In a set of carefully monitored optimisation reactions, low conversions were observed when CuBr$_2$ was employed, which is due to the complexation of the thioester with Cu catalyst. Nevertheless, once CuBr$_2$ is replaced with an iron based deactivator, full conversion for the homopolymerisation of ethyl thioacrylate is achieved. In a next step, the polymerisation conditions for an ethyl thioacrylate and a methyl acrylate block copolymer are optimised. The obtained block copolymer was subjected to an amidation reaction to obtain an all-acrylic copolymer, consisting of an acrylate, a thioacrylate and an acrylamide.

Introduction

Advances in synthetic strategies and polymerisation techniques have reached a point that makes pre-design and tailoring of application specific polymers possible. Unusually complex polymer structures can be obtained by a plethora of techniques available. For example, SET-LRP has proven to be a useful polymerisation technique in the synthesis of random and multiblock copolymers, as well as star shaped[1–3] or other branched polymers,[4] which can be readily obtained in an organic or aqueous medium[5–9] or even in the presence of oxygen.[10–12] While a range of initiators can be employed, the core structural features remain the same.[13,14] In a typical SET-LRP, it is proposed that Cu(I) species disproportionate in the presence of a ligand to "nascent" Cu(0) (activator) and Cu(II)-halide (deactivator) to mediate the polymerisation. The actual mechanism is however under debate and therefore out of the scope of this study.[15–17] Depending on the system, an ester or an amide based initiator is typically utilized, which mainly differs in their polymerisation kinetics and monomer compatibility.[13,18] Recently, a new class of initiators that is based on thioesters was also reported.[19] The fundamental building blocks are available in a vast range, such as (meth)acrylates, (meth)acrylamides, and styrenic derivatives, and can

be polymerized under a variety of conditions.[20,21] Consequently, monomers with functional groups that allow further functionalisation towards the desired application are extremely sought for. The thioester group represents such an example, and hence numerous studies have been reported which focus on its implementation in a polymer and further functionalisation. In general, a thioester can be incorporated into a polymer by employing a thioester functional initiator, by polymerizing a thioester containing monomers or by post modification functionalisation of a polymer.[22–25] One such approach that directly gives access to thioesters is the polymerisation of thioacrylate monomers. The current understanding of their polymerisation properties is limited to only a handful of reports which date back to the 1950s.[26] For example, Kawasaki and coworkers reported the synthesis of alkyl thioacrylates and their polymerisation *via* anionic polymerisation.[27] In another report, Hadjichristidis *et al.* prepared thiomethacrylates and utilized these for free radical polymerisation.[28–30] Recently, our group has investigated the polymerisation of different thioacrylates *via* reversible addition–fragmentation chain transfer (RAFT) polymerisation, resulting in a polymer with a high density of thioester functionality.[31] It was found that thioacrylates (TAs) resulted in well-defined polymers with predictable kinetics. While RAFT was concluded to be a suitable method to obtain copolymers of TAs, their polymerisation *via* any other controlled radical polymerisation (CRP) technique has not yet been reported and requires to be investigated for a better overall understanding of their compatibility and polymerisation behaviour.

Herein, we report the polymerisation of thioacrylates under "typical" SET-LRP conditions. Initially, the homopolymerisa-

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tion conditions were optimized by changing different variables such as $[M]:[I]$ (DP) and deactivator concentration. Furthermore different metal halide deactivators were employed to minimise any metal interaction to the ambidentate thioester and to achieve high monomer conversions.[32,33] With the help of the obtained results, a well-defined block copolymer of ethyl acrylate and ethyl thioacrylate (**ETA**) was prepared. Finally, this polymer was purified and amidation with benzylamine on thioacrylate was carried out to result in an "all-acrylic" polymer.
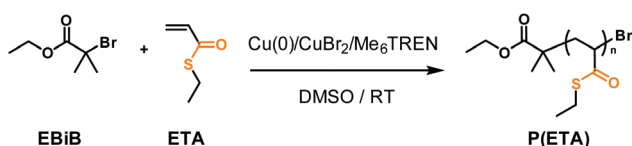
Results and discussion

Homopolymerisation of ethyl thioacrylate and optimisation reactions

Thioacrylates are the thioester equivalents of acrylates and acrylamides. By varying DP, the number of thioester units along a polymer chain can be targeted, allowing control over the thermal and physical properties of the polymer. In order to investigate their kinetics under metal mediated polymerisation techniques, typical SET-LRP conditions were employed. A series of optimisation reactions for the polymerisation of **ETA** using ethyl α-bromoisobutyrate (**EBiB**) were carried out (Scheme 1 and Table 1). Samples were taken periodically during the screening reactions and analysed to determine the conversion and molecular weight distribution *via* NMR spectroscopy and GPC. Analogous thioacrylate and acrylate monomers are shown to polymerise with similar kinetic rates, which displays the ease of thioester incorporation in a polymer.

Initially, the reaction conditions for the polymerisations were kept constant at $[Monomer]:[EBiB]:[Me_6TREN] = 10:1:0.19$ (Table 1).

Interestingly, the first order kinetic plot for the polymerisation of **ETA** (entry **P1**) displays a linear correlation for the initial four hours ($k_p^{app} = 5.283 \times 10^{-5}$ s^{-1}), after which the linear fit levels off to a horizontal line at a monomer conversion of 60%, yielding a polymer with $M_{n,GPC} = 4000$ g mol^{-1} and PDI = 1.11 (Fig. 1).

A linear dependence of $\ln[M]_0/[M]$ *vs.* time indicated first order kinetics with respect to the monomer concentration between 30 and 240 minutes, while M_n increased linearly with conversion and PDI values remained narrow (1.07–1.15) throughout the reaction. However, no further increase in con-

Table 1 Summary of the results obtained from the optimisation of **ETA** polymerisation reactions under various reaction conditions

Entry	DP$_{ETA}$	[CuBr$_2$]:[I]	[Me$_6$TREN]:[I]	Cu(0) (cm)	T (°C)	ρ^a (%)
P1	60	0.1	0.19	4.0	25	60
P3	20	0.1	0.19	4.0	25	80
P4	10	0.1	0.19	4.0	25	92
P5	20	0.2	0.19	4.0	25	50
P6	20	0.1	0.38	4.0	25	81
P7	20	0.1	0.19	4.0	25	80
P8	20	0.1	0.19	4.0	25	80
P9	20	0.1	0.19	4.0	40	91
P10	20	0.1	0.19	10.0	25	90
P11	10	0.1 CuCl$_2$	0.19	4.0	25	86
P12	10	0.05	0.19	4.0	25	86
P13	10	0.1 FeBr$_2$	0.19	4.0	25	100
P14	10	0.1 FeBr$_3$	0.19	4.0	25	100
P15	10	0.1 FeBr$_3$	0.19	4.0 Fe(0)	25	30
P16	10	0.1 FeBr$_3$	0.19	—	25	87

Note that **P1** is obtained after kinetic sampling, while entries **P3**–**P16** were allowed to polymerise uninterruptedly for 16 hours in DMSO at a monomer solvent ratio of 1:2 (*v/v*) except for **P7** (1:8, *v/v*) and for **P8** (TFE, 1:2, *v/v*). ^{a} Conversion determined *via* ^{1}H NMR spectroscopy.

a)

b)
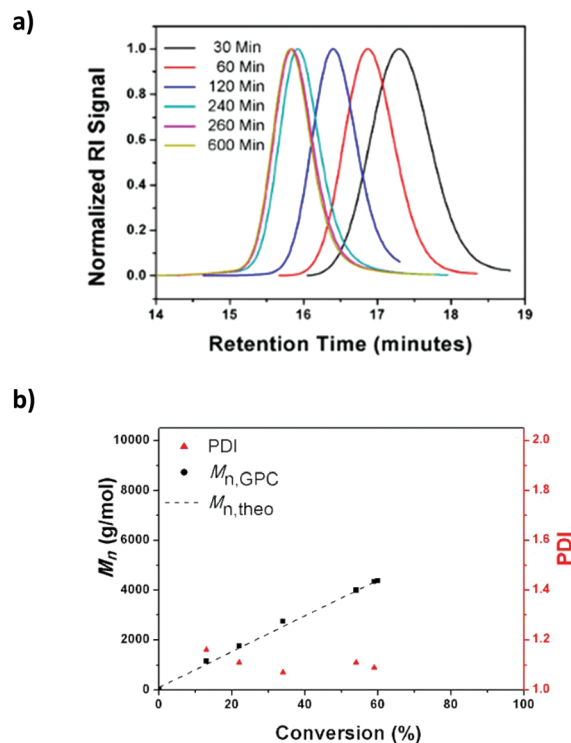
Fig. 1 (a) GPC traces of the homopolymerisation of **ETA** with a linear initiator (**EBiB**) at DP = 60 in DMSO (**P1**) and (b) M_n *vs.* conversion plot for **P1**. Black symbols represent $M_{n,GPC}$, red symbols their PDI, and the dashed line represents the respective $M_{n,theo}$ (see also Fig. S1†).

Scheme 1 General conditions for the polymerisation of **ETA** *via* SET-LRP. **P1** was obtained using **EBiB** with [ETA]:[I]:[CuBr$_2$]:[Me$_6$TREN] = 60:1:0.1:0.19 while **P2** was obtained using a pentaerythritol based tetra functional star initiator (PE-Br$_4$) with [ETA]:[I]:[CuBr$_2$]:[Me$_6$TREN] = 60:1:0.4:0.76 in DMSO at RT.

version or in the average molecular weight could be observed after 360 minutes. Similarly, the homopolymerisation of **ETA** using PE-Br$_4$ presented remarkably low dispersities throughout the polymerisation (1.04–1.08). However, the conversion of **P2**

stopped at 65% as for **EBiB**, with no detectable increase in the molecular weight even after 24 h ($M_{n,GPC}$ = 3300 g mol^{-1}, PDI = 1.08, Fig. S2†).

With the advances in novel polymerisation techniques in recent years, it was shown that interesting properties can be gained by simply iteratively polymerising different functional monomers to block copolymers.[34] However, to be able to truly obtain block copolymers, conversions near or equal to 100% need to be obtained for every block prior to *in situ* chain extension, avoiding exhaustiveness in between purification steps. To be able to obtain a block copolymer of **ETA**, we aimed next for lower [M]:[I] ratios in order to attain full conversion, before carrying out further optimisation. Hence, the DP was gradually decreased to 20 and 10, which afforded an increase in conversion to 80% and 92% respectively (entries **P3** and **P4**, Fig. S3†). In addition, doubling the CuBr$_2$ concentration compared to **P3** resulted in a monomer conversion of 50% with a broader distribution over the same time period (**P5**, $M_{n,GPC}$ = 1300, PDI = 1.13, Fig. S4†). In another attempt to increase the conversion, the ligand concentration was increased from 0.19 (**P3**) to 0.38 eq. for **P6**; however, the conversion remained at 81% (**P6**, $M_{n,GPC}$ = 1600 g mol^{-1}, PDI = 1.17, Fig. S5†), which is further confirmed by similar $M_{n,GPC}$ values.

Although the dilution of the monomer concentration leads to slower polymerisation kinetics or even lower conversion, the amount of DMSO was increased 3-fold to 8:1 (v/v) in **P7**, in order to exclude any possible solubility issues.[35,36] At the same time, another polymerisation was carried out in 2,2,2 trifluoroethanol (TFE) as Percec and coworkers reported TFE to be a good alternative to DMSO which yields "nascent" Cu(0).[37–39] Neither a change in the solvent amount nor the use of TFE as a solvent attained a conversion higher than 80% (**P7**, $M_{n,GPC}$ = 1200 g mol^{-1}, PDI = 1.10 and **P8**, $M_{n,GPC}$ = 1300 g mol^{-1}, PDI = 1.43, Fig. S6†). Furthermore, a deviation in polymerisation control was indicative by a much broader GPC signal for **P8** (Fig. S7†). A slight increase in conversion was only observed, when the reaction temperature was increased to 40 °C for **P9** (Fig. S8†) or when a longer piece of the Cu(0)-wire (10 cm) was used in **P10** (Fig. S9†), reaching 90% monomer conversion in both polymerisations.[6] Furthermore, CuBr$_2$ was replaced with CuCl$_2$ in order to investigate the effect of the nature of the deactivator using 0.05 eq. and 0.1 eq. It was found in both cases that the conversions slightly dropped (86%); however they were not dependent on the individual CuCl$_2$ concentrations used (compare entries **P11** and **P12** to **P3**). This was found to be in agreement with previous reports, considering the higher deactivation rate constant of –Cl based deactivators.[40] However, when iron based deactivators, namely FeBr$_2$ or FeBr$_3$, were used, 100% monomer conversions were reached (**P13** and **P14** respectively). The obtained polymers were analysed *via* GPC and were found to be well defined polymers with low dispersities (**P13**, $M_{n,GPC}$ = 1290 g mol^{-1}, PDI = 1.17 and **P14**, $M_{n,GPC}$ = 1360 g mol^{-1}, PDI = 1.21, Fig. S12 and S13†).

These findings caused speculation for a potential thioester-copper complexation or interaction that could be decreasing the reactivity of the polymerisation system, hence resulting in

low conversions (compare entries **P4** and **P13**).[32,33] Conversion dropped much lower, also when the Cu(0)-wire was replaced with a 4 cm Fe(0) wire in the presence of FeBr$_2$ (**P15**), displaying no control over dispersity (Fig. S14,† $M_{n,GPC}$ = 21 400 g mol^{-1}, PDI = 3.21). To our surprise, when the same experiment was repeated without the Fe(0)-wire (**P16**), a higher monomer conversion of 87% was obtained. The GPC analysis additionally revealed a narrower molecular weight distribution with PDI = 1.25 (Fig. S15†).

From the above obtained results, it was concluded that only the use of iron halide in the presence of a Cu(0) wire resulted in quantitative monomer conversion for the polymerisation of thioacrylates with low dispersities. Therefore, different metal halides were compared under a set of identical reaction conditions, for the polymerisation of **ETA** and ethyl acrylate (**EA**), which are discussed further in the following.

Kinetic comparison of different metal halides for the homopolymerisation of ethyl acrylate and ethyl thioacrylate

While Fe-based deactivators helped to increase the monomer conversion for a thioacrylate based monomer, their influence as metal halides on acrylates compared to CuBr$_2$ was also investigated to be able to draw a comparison. For this purpose, kinetic investigation for ethyl acrylate polymerisation (**P17–P20**) and ethyl thioacrylate polymerisation (**P21** and **P24**, Fig. 2) was carried out and is reported in Table 2. When **ETA** was polymerised with 0.10 eq. of CuBr$_2$ (**P21**), the reaction was very poorly defined, as evidenced by GPC traces with unsymmetrical distribution at higher conversions (Fig. S16†). The polymerisation resulted in significant loss over the control for the homopolymer, characterised by incomplete conversion (90%) and by significant high molecular weight signals. GPC analysis furthermore revealed a steady increase of the measured molecular weight with increasing conversion retaining relatively low dispersities below 80% conversion. However, after 80% conversion was reached, the molecular weight stagnates and broader distributions are detected (Fig. S17†). When CuBr$_2$ was replaced with FeBr$_2$ for **P22**, GPC analysis revealed narrow, symmetrical molecular weight distributions with dispersity indices around 1.10. Furthermore, the measured molecular weight constantly increased until full monomer conversion was reached (Fig. S18†). In a next experiment, CuBr$_2$ was replaced with FeBr$_3$ for **P23** and resulted also in full conversion of **ETA**, following a non-linear increase of (ln[M]$_0$/[M]) over time (Fig. S19†). When CuBr was employed in a further experiment for **P24**, GPC analysis revealed no shift of the GPC traces to higher molecular weights and the polymerisation did not proceed to full conversion (Fig. S20†).

In general, it was found that for acrylates, all metal halides could be employed interchangeably (**P17**, **P18**, **P19** and **P20** all resulting in $M_{n,GPC}$ = 1400 g mol^{-1}, PDI = 1.10). However, it should be noted that a difference in the time required to reach full conversion was observed, where **P17** required 105 minutes, **P18** 150 minutes and **P19** 180 minutes. Additionally, for ethyl acrylate, the kinetic rate constants appear to be similar, yet there is a notable difference in the induction period, ranging
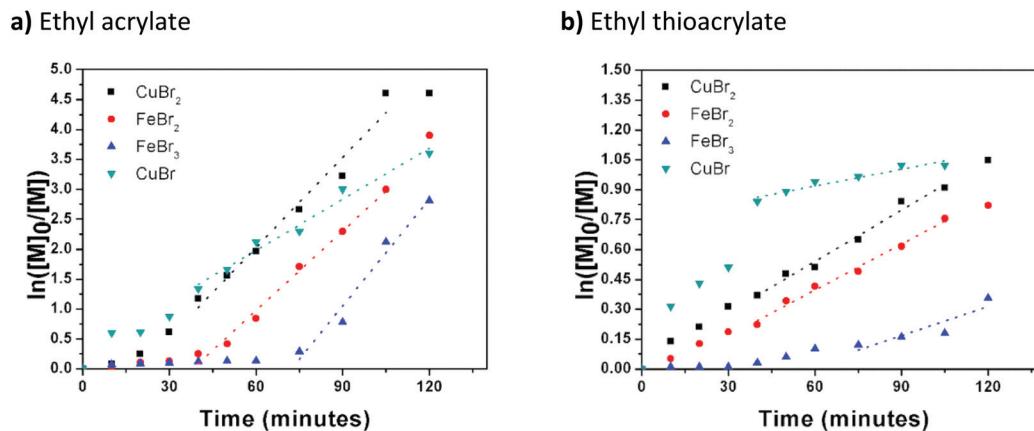
a) Ethyl acrylate

b) Ethyl thioacrylate

Fig. 2 First order kinetic plot of different deactivators (0.1 equivalents) for [Monomer] : [EBiB] : [Me_6TREN] = 10 : 1 : 0.19, (a) using ethyl acrylate and (b) ethyl thioacrylate. See Fig. S21† for plots up to 480 minutes.

Table 2 Overview of the carried out polymerisations with different metal halides for ethyl acrylate and ethyl thioacrylate (**P17–P24**)

| Entry	Monomer	Metal halide	k_p^{app} (s^{-1})	Induction period (min)	Time for quantitative conversion (min)
P17		CuBr$_2$	8.36×10^{-4}	20	105
P18		FeBr$_2$	7.36×10^{-4}	50	150
P19		FeBr$_3$	9.90×10^{-4}	75	180
P20	**EA**	CuBr	4.74×10^{-4}	20	>120
P21		CuBr$_2$	1.43×10^{-4}	Not observed	>480
P22		FeBr$_2$	1.29×10^{-4}	Not observed	360
P23		FeBr$_3$	8.08×10^{-5a}	40	480
P24	**ETA**	CuBr	4.70×10^{-5}	Not observed	n/a

^{a} For a more accurate comparison, the rate reported is determined from the initial linear regime between 40 and 105 minutes (see Fig. S21b †).

from 20 minutes with CuBr and CuBr$_2$ to 75 minutes for FeBr$_3$.

Once monomer conversion started, the polymerisation rates were found to be independent of the deactivator used. A comparable trend was observed for the initial 120 minutes of the polymerisation for ethyl thioacrylate (Fig. 3). For example both **P21** and **P22** proceed nearly identical, with comparable polymerisation rates and with no evidence for an induction period. After 150 minutes however, a steeper second linear regime appears for **P22** leading to quantitative conversion, while **P21** plateaus for the next *ca.* 3 h, whereafter no polymerisation occurs. **P23** on the other hand is initially observed to have an induction period of 40 minutes, after which it proceeds to full monomer consumption within 8 hours. From these results, it can be concluded that the biggest difference observed for ethyl acrylate was in the duration of the induction period, while the polymers resulted in nearly identical distributions with comparable k_p^{app} values.[41,42] For ethyl thioacrylate however, the polymerisation using CuBr$_2$ was found to stop at about 92%. In contrast, iron based deactivators were found to be more suitable, as they allowed monomer conversion to reach 100%, resulting in well-defined polymers. From the above two results, FeBr$_2$ showed more controlled characteristics, as the kinetic plots displayed distinct linear regimes compared to a sigmoidal trend obtained with FeBr$_3$. In short, while the presence of

FeBr$_2$ allowed the polymerisation of thioacrylates, CuBr$_2$ was found to be unsuitable. Encouraged by these results, the extension of the monomer library was tried using dimethyl acrylamide (DMA). DMA is a well-known acrylamide, which is preferably polymerised *via* RAFT or other CRP techniques,[43] due to unfavourable side reactions (*e.g.* with the catalyst) and terminations occurring in transition metal mediated (TMM) polymerisations.[44,45] In an effort to obtain PDMA, the optimised conditions for **ETA** were used. Unfortunately, the conversion of DMA only reached 21% with CuBr$_2$ (**P25**), 49% with FeBr$_2$ (**P26**) and 45% with FeBr$_3$ (**P27**). The low conversion obtained for DMA was predictable from previous reports about the inefficient polymerisation of acrylamides *via* TMM that can be found throughout the literature. On the other hand, a complexation with CuBr$_2$ seems to be having a more negative impact on the polymerisation, whereas higher conversions are reached, when iron based halides are used. It should be noted that a similar trend was observed for thioacrylates as mentioned above.

Incorporation of monomers, which are difficult to polymerise, is typically achieved *via* protecting groups or post polymerisation functionalisation. Thiol bearing monomers for example can be converted into thioesters to avoid their interference with the polymerisation system, which can be hydrolysed back to their free thiols after the completion of the polymerisation.[22]
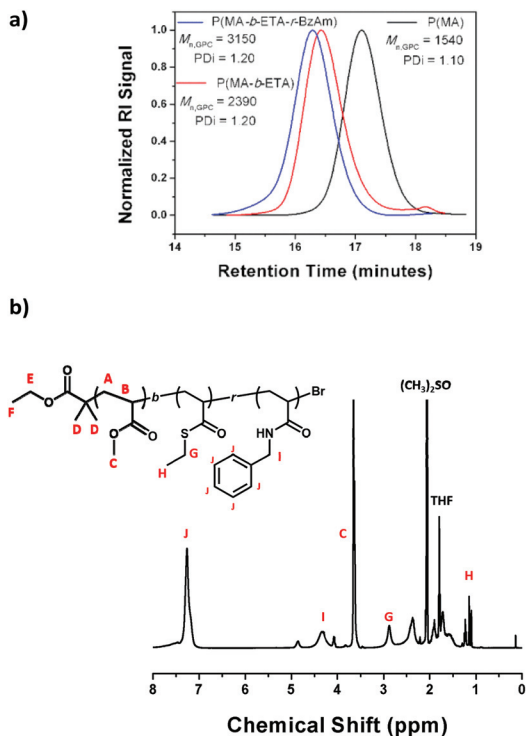
Fig. 3 Overlay of the obtained GPC traces for the synthesis of (a) **P37** and (b) "all-acrylic" polymer **P38**, while (c) displays the ^{1}H NMR spectrum obtained for **P37** after purification.

Similarly, anchoring points or functional groups can be inserted along a polymer backbone that can be transformed into other chemical moieties.[46] With the obtained results described above, we theorised that not only would it be possible to convert poly(ethyl thioacrylate) into a poly(acrylamide) *via* amidation, but also its copolymer with an acrylate could be transformed into an "all-acrylic" polymer consisting of three different building blocks: acrylates, acrylamides and thioacrylates along a single polymeric chain. Since such a polymer has not yet been reported, the investigation of its characteristics could unveil interesting new properties. For this hypothesis, the block copolymerisation of an acrylate with a thioacrylate required to be optimised, which is further discussed in the following.

Chain extension of P(MA) with ETA

Under SET-LRP conditions, quantitative conversions for ethyl thioacrylate and ethyl acrylate can be reached. The level of livingness/chain end fidelity can be further investigated by *in situ* chain extension. For this purpose, kinetic investigation on the homopolymerisation of methyl acrylate (MA) with either CuBr$_2$ (**P28**) or FeBr$_2$ (**P29**) was performed. ^{1}H NMR analysis revealed full conversion within 120 minutes for **P28** and 140 minutes for **P29** (Fig. S23 and S24† respectively). Furthermore, an initial induction period of 20 and 30 minutes and an almost a linear dependence of $\ln[M]_0/[M]$ *vs.* time were observed, indicating first order kinetics with respect to the monomer concen-

tration. As no difference for MA was observed, FeBr$_2$ was chosen to be used, since earlier results obtained displayed better polymerisation conditions for thioacrylates. Chain extension by the addition of **ETA** in DMSO after 16 hours furnished higher molecular weight polymers with an increase in dispersity to 1.40 for **P30** with 80% conversion of the second block. A similar chain extension was performed, adding an extra ligand and FeBr$_2$ to the second block of **ETA** in **P31**. The addition of extra FeBr$_2$/Me$_6$TREN allowed the second block of **ETA** to reach higher conversions (91%), while retaining a narrow polydispersity (Fig. S22†). Therefore, conditions for **P31** were applied for a chain extension with 5.00 equivalents of **ETA** (**P32**) reaching a 97% monomer conversion for the second block. GPC analysis revealed a shift towards higher molecular weights and a negligible increase in dispersity to 1.10 for **P32** (Fig. S25†).

Chain extension by addition at 100 minutes with 60.0 equivalents of **ETA** in DMSO with an additional ligand and FeBr$_2$ furnished higher molecular weight polymers with almost a 6 fold increase in the molecular weight. From the GPC traces it is visible that all chains have initiated during the chain extension, which can be concluded from the disappearance of the signal for the first block in the region between 17 and 19 minutes. The second block only reached a monomer conversion of 78%, while a broadening of the dispersity was observed (**P33**, $M_{n,GPC}$ = 6300, PDI = 1.76). An overlay of the first and second block traces obtained by GPC is depicted in Fig. S26.†

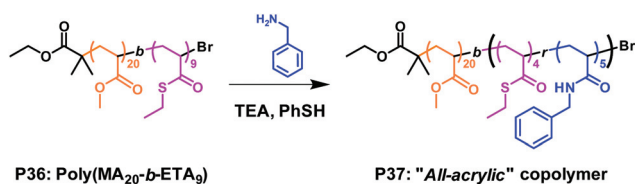### Chain extension of P(ETA) with MA

To investigate the livingness of **P(ETA)** under SET-LRP conditions, the reverse strategy was followed by the chain extension of **P(ETA)** with MA. Additionally, the amount of FeBr$_2$ and ligand was varied to explore the effects for the second block under the conditions applied. For this, the *in situ* chain extension of **P(ETA)** (**P34**) with 60 equivalents of MA was complemented by the addition of 0.05 : 0.09 (**P35a**), 0.10 : 0.19 (**P35b**) and 0.20 : 0.38 (**P35c**) of [FeBr$_2$] : [Me$_6$TREN]. In all cases, **P(ETA)** could be chain extended with MA, but GPC analysis additionally revealed that not all chain ends of **P(ETA)** initiated during the chain extension. When a low concentration of [FeBr$_2$] : [Me$_6$TREN] = 0.05 : 0.09 was used for **P35a**, full conversion for the second block was obtained after 24 hours, with a small high molecular weight signal appearing at 14 minutes (Fig. S27a†). Typical conditions of [FeBr$_2$] : [Me$_6$TREN] = 0.10 : 0.19 yielded a broader peak after the chain extension and a lower conversion (88%) for the second block, with no signal in the high molecular weight region (**P35b**, Fig. S27b†). This was not the case for **P35c**, when a higher concentration was used with [FeBr$_2$] : [Me$_6$TREN] = 0.20 : 0.38. The increase of FeBr$_2$ and ligand resulted in an additional and significantly more evident peak around 14 minutes in the higher molecular weight region, attributed to the occurrence of bimolecular coupling reactions (Fig. S27c†). Nevertheless, ^{1}H NMR spectroscopy revealed full conversion for the second block in 24 hours.

Post-polymerisation amidation and synthesis of an "all-acrylic" polymer

As discussed above, thioesters allow further modification, when an amine functional molecule is presented. Typically, activated ester monomers are used which can be highly reactive towards amidation reactions. For example, Theato and coworkers have employed a series of methacrylic polymers with a range of ester activities.[47] While poly(pentafluorophenyl methacrylate) could undergo full amidation at 50 °C, poly(methyl methacrylate) only reached 20% amidation even at temperatures as high as 120 °C. In another study, Sumerlin and coworkers reported that amidation could be carried out even on non-activated methacrylic polymers, if triazabicyclodecene (TBD) is employed as the catalyst under reflux conditions.[48] Recently, Hoogenboom and coworkers expanded the library that can be employed for the amidation of P(MA), by investigating a range of amines to be able to incorporate functionalities into the side chain that radical polymerisation techniques otherwise would not tolerate.[49] Thus investigating the amidation possibilities on poly(thioacrylate)s was of outmost interest. For this purpose, the chain extension of **P30** was repeated in a next experiment to yield a polymer for further modification. FeBr$_2$ was employed to chain extend P(MA) with **ETA** to poly(MA$_{20}$-b-ETA$_{10}$) (**P36**, $M_{n,GPC}$ = 2400 g mol^{-1}, PDI = 1.20) resulting in 97% monomer conversion. Block copolymer **P36** was used further for partial amidation, with conditions that were previously optimised on a sequence controlled oligomer (Scheme 2).[25]

To the pure polymer (previously dialysed against THF), 2.5 eq. of benzylamine per thioester was added in the presence of trimethylamine and thiophenol to obtain partial amidation at room temperature. The relatively mild conditions allow for modification with only thiol as a side product, which can be dialysed out or even readily removed under reduced pressure. In order to be able to determine the final polymer composition, a small sample was submitted to analysis via ^{1}H NMR spectroscopy (Fig. 3). Comparison of the benzyl peaks appearing between 7 and 7.5 ppm and the –CH$_3$ signals of P(MA) around 3.6 ppm revealed a $ca.$ 55% conversion for the amidation reaction. From the spectrum, it was also found that the methyl acrylate fraction did not change over the course of the amidation, therefore proving that amidation can selectively be carried out on the thioacrylate block, even in the presence of methyl acrylate. Thus, the incorporation of amines via the thioester bond and the first synthesis of an "all-acrylic" copolymer **P37** are achieved (Table S7†).

Conclusions

In this study, the first synthesis of linear and star-shaped poly (ethyl thioacrylate) via SET LRP is demonstrated, which resulted in very well defined polymers, yet with limited monomer conversions. Due to this, the polymerisation conditions were optimised in a series of carefully monitored experiments, in which an interaction between the copper halide and thioester was evident. Polymerisations with FeBr$_2$ instead resulted in full conversion. Using newly established conditions, MA was polymerised and chain extended with ethyl thioacrylate. The purified polymer was finally subjected to an amidation reaction allowing direct access to the first example of an "all-acrylic" copolymer. In the future, we believe this class of copolymers to potentially reveal new physical and thermal properties, as well as their use to be of great interest for both industrial and academic applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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