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Nitroxide-mediated polymerisation of thioacrylates and their transformation into poly(acrylamide)s†

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One long-standing challenge in polymer science is the development of transformation reactions, in which the conversion of a specific functional group to another is targeted. For this purpose, a thioester polymer consisting of thioacrylate monomers has been prepared *via* nitroxide-mediated polymerization and its kinetics has been studied for the first time. The copolymerization behavior of butyl thioacrylate with PFS was investigated in detail and compared to the copolymerization of butyl acrylate and PFS. Finally, a series of modification reactions were carried out using different amines and alcohols, in an attempt to transform the thioacrylate monomer into an acrylamide or acrylate, respectively. The established conditions allowed one to obtain poly(acrylamide)s *via* post polymerization functionalization in a versatile and efficient way, which is why this process is believed to be widely used by polymer chemists.

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Introduction

Within the field of chemical synthesis, transformation reactions play a pivotal role in which a compound is transformed into an entirely different functional group. In fact, a considerable number of these reactions focus on reactions with amines. In particular, amide-bond formation is a common occurrence in the synthesis of pharmaceuticals, natural products and fine chemicals.¹ The ability to convert a functional group into an amide remains an important endeavour with a remarkable impact, as it allows straightforward access to amide-based polymers that mimic biomacromolecules, aiding to understand their biological functions.² In addition, many novel transformation reactions on polymers have been reported, which opened new avenues towards novel value-added materials.³

Transformation reactions on polymers are typically desired in two main situations. In the case of some monomers, the functionality has to be protected with protecting groups prior to polymerisation, in order to avoid possible side reactions. For example, some reactive monomers cannot be polymerised due to their interference with the polymerisation equilibrium. They are deprotected after polymerisation, resulting in the end product (*e.g.* acidolysis of poly(*tert*-butyl acrylate) to poly(acrylic acid) *via* ATRP).⁴ On the other hand, modification reac-

tions present a route to a polymer, when its monomer is not readily available. In such a case, the monomer or its functional group would be transformed *via* post polymerization modification to the desired polymer (*e.g.* amidation of thioesters).⁵ Possible transformation reactions that are widely employed include addition reactions such as thiol-ene,⁶ thiol-yne,⁷ Michael addition^{8,9} or cycloadditions, as well as exchange reactions.¹⁰

Although numerous functional groups can undergo transformation, one common example is the transformation of esters. Ester-containing monomers can be easily polymerised to yield reactive precursors, where a range of amines from natural or commercial sources can be employed as nucleophiles.¹¹ Prominent examples of esters include pentafluorophenyl (PFP) esters, *N*-hydroxysuccinimide (NHS) ester monomers,¹² pentafluorophenyl ester-based acrylates (PFPA) and methacrylates (PFPMMA).¹³ Moreover, thiolactones (TLa)^{14,15} and vinyl benzoates (PFP4VP) are also widely represented.

As ester transformations typically require extended reaction times and high temperatures, more efficient catalytic approaches have been reported. For example, their catalytic activation with a nucleophilic organocatalyst for primary amines and alcohols has been recently reported using 1,5,7-triazabicyclo[4.4.0]undec-5-ene (TBD).¹⁶ A base-catalysed amidation with an exogenous alcohol-derived additive to form an active ester *in situ* has also been reported.¹⁷ On the other hand, Hillmyer and co-workers have reported a metal-free nucleophilic substitution with amines and alcohols on an activated amide polymer of di(Boc)-acrylamide (DBAm).¹⁸ Nevertheless, the use of strong bases and harsh reaction conditions (*i.e.* high temperatures and an excess amount of reactants) was inevitable.

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Another group of polymers that can be transformed are represented by thioester-containing polymers. The versatility of thioesters with respect to their functionalisation with different compounds has already been proven. Their modification with thiols, azides, amines and cysteine-containing peptides to enable modification *via* pathways such as ligation, amidation or exchange reactions was previously discussed elsewhere.¹⁹ Although thioesters have been a central theme in organic chemistry, only a limited number of investigations on the modification of thioester-containing polymers have been reported.

Herein, we describe amidation on poly(thioacrylate)s, inspired by a report on a metal-free, thiol-catalysed amidation of thioesters²⁰ and by a similar approach in the solid phase through thiol-catalysed substitution.¹⁴ The polymers of thioacrylates were prepared *via* nitroxide-mediated polymerisation (NMP), which has been exemplified herein for the first time. The reaction kinetics of their homopolymerisation and copolymerisation behaviour with a styrene derivative (2,3,4,5,6-pentafluorostyrene, PFS) as a second type of functional monomer was studied *via* periodic sampling. The kinetic studies of the reaction between primary amines and thioacrylates were investigated using benzylamine and poly(ethyl thioacrylate) as model compounds. This study was expanded further by employing isopropylamine and benzyl alcohol in the presence of thiophenol and base for the transformation of the thioester moiety.

Results and discussion

Low-temperature nitroxide-mediated polymerisation

The NMP process typically requires relatively high temperatures to allow the reversible dissociation of the alkoxyamine product. However, in recent years much effort has been put into the development of nitroxide initiators for the controlled polymerization of monomers at lower temperatures than the temperature range of 110–120 °C that is typically employed.^{21–24} *N*-(*Tert*-butyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*O*-(2-carboxylprop-2-yl)-hydroxylamine (SG1-MAMA or BlocBuilder™) is an efficient alkoxyamine initiator for the polymerisation of a broad variety of different monomers (*e.g.* styrenics, acrylamides, and acrylates),^{25–30} with a suggested reaction temperature ranging from 90 to 120 °C.^{31,32} Butyl acrylate (BuA) is a representative short alkyl chain acrylic ester often polymerised *via* NMP and many studies carried out under various conditions have been reported to date.^{33–36} BuA has therefore been used in this study as a model acrylate to compare it with its thioester counterpart butyl thioacrylate (BuTA) and polymerized at moderate and higher temperatures using SG1-MAMA as the nitroxide initiator (see the ESI for the full Experimental section). The polymerisation kinetics was initially followed at 70 and 120 °C in DMF (Fig. 1) using $[M]_0 : [SG1-MAMA]_0 = 50 : 1$ (**P1–P4**). The semi-logarithmic kinetic plots for BuTA and BuA at 70 °C and 120 °C are shown in Fig. 1B–C, respectively, from which the

apparent propagation rates (k_p^{app}) can be estimated using the gradients from the initial linear region. Conversions were calculated *via* nuclear magnetic resonance (NMR) spectroscopy by comparing the *CH*- resonance of the vinyl group at around 5.50 ppm (residual monomer) with the side chain *CH*₃- signal at around 1.00 ppm.

The k_p^{app} for the homopolymerisation of BuTA (**P1**) shows a 5.4-fold higher rate ($2.75 \times 10^{-5} \text{ s}^{-1}$) compared to its acrylate counterpart BuA (**P2**, $5.06 \times 10^{-6} \text{ s}^{-1}$) and presented a unimodal molecular weight distribution throughout the reaction. However, it did not proceed to full monomer conversion, stopping its increase after 240 minutes at 59% ($M_{n,GPC} = 3500 \text{ g mol}^{-1}$, PDI = 1.78). In comparison, the polymerisation of BuA in the same time period resulted in a monomer conversion as little as 13% (**P2**) with no polymeric signal being detected *via* gel permeation chromatography (GPC), which is in agreement with the lower k_p^{app} value (Tables S1 and S2†).

Next, the polymerisation temperature was increased to 120 °C in a further attempt to obtain higher monomer conversions. Within 2 hours, BuTA already reached full conversion with a dispersity of 1.67 (**P3**, $M_{n,GPC} = 4300 \text{ g mol}^{-1}$), whereas BuA remained at 91% (**P4**, $M_{n,GPC} = 3300 \text{ g mol}^{-1}$). While the experimental values ($M_{n,GPC}$) were closer to the calculated values ($M_{n,theo}$) for **P3**, an increased deviation over time was evident for **P4** that was attributed to the calibration standards used (Tables S4 and S5†), which was found to be in agreement with previous reports.^{37,38}

As the dissociation of the C–ON bond is an endothermic process, an increase in temperature will enhance the rate of the dissociation of C–ON and subsequently increase the rate constant *K*. Hence, for both BuA and BuTA, an increase in k_p^{app} was observed when the temperature was increased to 120 °C, as expected. In fact, this increase led to a 1.3-fold higher value for BuTA, while the increase for BuA was more remarkable. Moreover, this observation shows that the propagating secondary radical is less stable with thioacrylates and therefore propagates at a faster rate than with acrylates. Finally, the linearity between the monomer concentration and time, at both temperatures, shows that thioacrylates can survive polymerisations at temperatures up to 120 °C and are compatible with NMP conditions.

Rate acceleration of pentafluorostyrene in NMP when copolymerised with thioacrylates

The alkoxyamine employed in the previous section enabled the controlled polymerisation of selected acrylates and thioacrylates. Monomer families compatible with SG1-MAMA include styrenes, acrylates and acrylamides, as well as 1,3-dienes and acrylonitrile-based monomers. Therefore, we investigated whether SG1-MAMA was also able to control the copolymerisation of a second functional monomer (pentafluorostyrene, PFS) to understand the kinetic effect of a thioacrylate comonomer on the system. In a series of kinetic experiments, PFS was copolymerised with BuTA, to yield a linear polymer (**P5**) with two functional monomers. Next, by copolymerising PFS with BuA (**P6**), the k_p^{app} values obtained from **P5** and **P6** could be

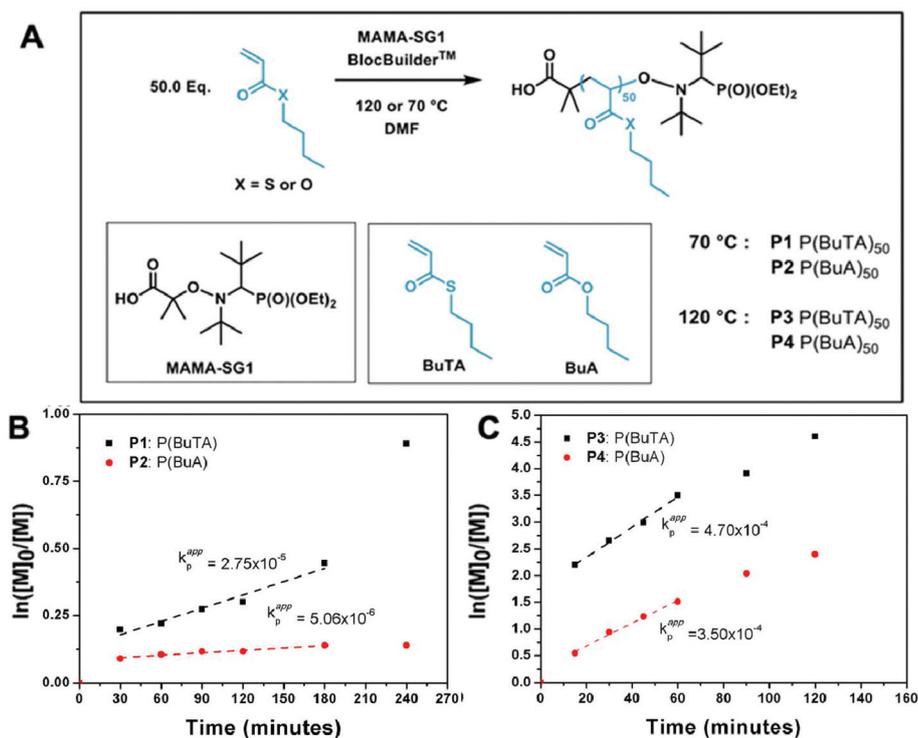


Fig. 1 (A) The reaction scheme for the NMP of butyl thioacrylate (BuTA, P1 and P3) and butyl acrylate (BA, P2 and P4), (B) semi-logarithmic kinetic plot of BuA and BuTA homopolymerisations at 70 °C, and (C) semi-logarithmic kinetic plot of BuA and BuTA homopolymerisations at 120 °C.

compared to gain better insight into the influence of different comonomers.

Choosing PFS has certain advantages. For example, it is commercially available and it is a widely used monomer for post polymerisation modifications.^{39,40} The *para*-fluorine atom of the PFS moiety is susceptible to a nucleophilic attack by alcohols, amines, phosphines, and to a range of sulfur-based compounds, particularly thiols. The incorporation of a thioacrylate into a PFS polymer will furnish a second functional group that is suitable for a nucleophilic attack and allows orthogonal modification. In the following part, the radical copolymerisation of BuTA with PFS (P5) and BuA with PFS (P6) was investigated (Fig. 2A) and the representative results are shown in Fig. 2B. Within an hour, well-defined poly(PFS-*r*-BuTA) and poly(PFS-*r*-BuA) copolymers were already obtained (Fig. 2C). From kinetic sampling, a significantly enhanced polymerisation rate was observed in P5, resulting in a polydispersity of 1.46. Interestingly, the copolymerisation of PFS with BuA resulted in a lower k_p^{app} value for both monomers, while retaining a lower dispersity of 1.27.

For instance, when butyl acrylate was employed as a comonomer, a lower conversion (10%) was obtained for PFS at 60 minutes in comparison with 94% when BuTA was employed as a comonomer (Fig. 2B). The apparent propagation rates in P5 were calculated as $3.35 \times 10^{-4} \text{ s}^{-1}$ and $4.96 \times 10^{-4} \text{ s}^{-1}$ for PFS and BuTA, respectively. For comparison, the propagation rates in P6 were calculated as $1.86 \times 10^{-4} \text{ s}^{-1}$ and $1.32 \times 10^{-4} \text{ s}^{-1}$ for PFS and BA. It is clear that the rate of propagation of

PFS was slowed down almost by half when BuA was used as a comonomer. This is reasoned with the class of the comonomer and its contribution to the overall propagation. Although BuTA polymerises faster than BuA, it is also believed that the more electrophilic nature of the thioester further enhances the copolymerization rate of PFS, resulting in a higher k_p^{app} .⁴¹ Critically, it should be noted that the decrease in polydispersity (P6) should not be solely attributed to the slower polymerization rate or lower temperature, but could also be reasoned with the type of comonomer used, as their homopolymers also resulted in different dispersities (see above P1–P4).

Transformation of poly(thioacrylate)s into poly(acrylamide)s via an amidation reaction

In order to investigate the modification of poly(ethyl thioacrylate) (PETA) with nucleophiles, the homopolymerisation of ethyl thioacrylate (ETA) was performed in DMF at 120 °C (P7, $[\text{M}]_0 : [\text{SG1-MAMA}]_0 = 20 : 1$), which reached full monomer conversion after 90 minutes (Fig. S7†). After the polymerisation, the reaction solvent was removed under reduced pressure to yield a pale yellow sticky polymer. The ¹H and ¹³C NMR spectra of the purified polymer P7 are shown in Fig. S8 and S9.† Specifically, a broad peak due to the CH₃- group (H_d) of the alkyl side group appears at δ 1.36, while a peak of the SCH₂- group that is next to the thioester side group (H_c) appears at δ 2.91. The backbone peaks for the CH- group (H_b) are visible at 2.61 ppm, while the neighbouring CH₂- group (H_a) appears between 1.76 and 1.99 ppm. Integration of the

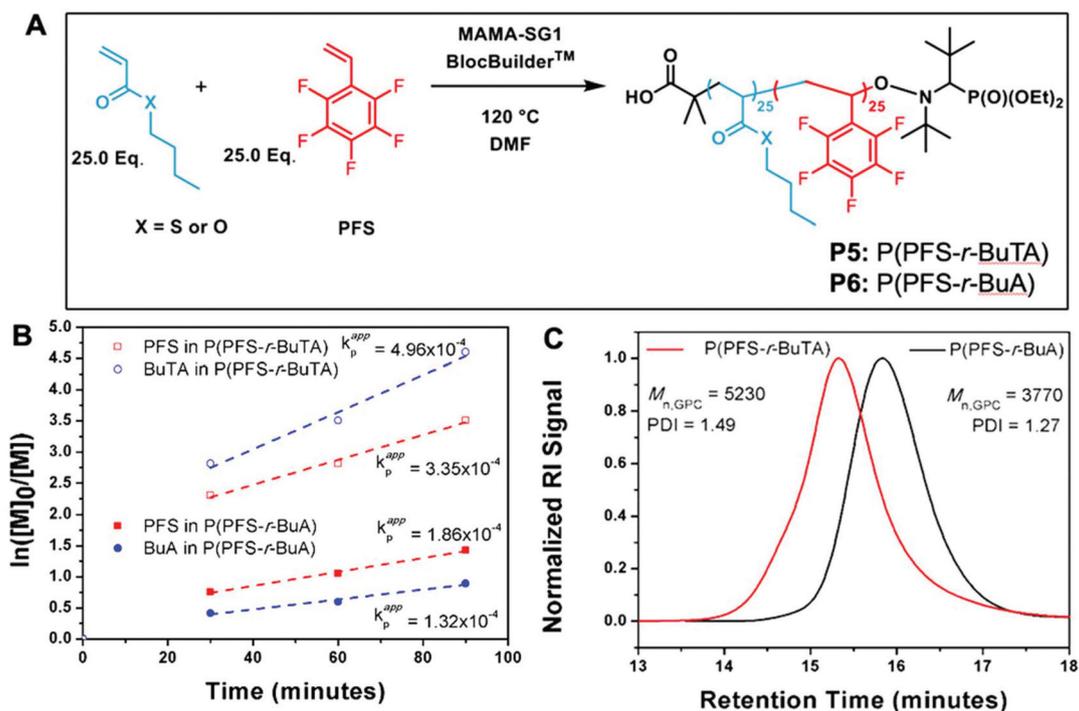


Fig. 2 (A) The reaction scheme for the NMP of BuTA or BuA with pentafluorostyrene (PFS, P5–P6), (B) semi-logarithmic kinetic plot of copolymerization reactions and (C) GPC traces of the random copolymers obtained for P5 and P6.

methyl peak at δ 1.36 and the CH - polymer backbone peak at 2.61 ppm shows that these protons are present in a 3 : 1 ratio, as expected. In the ^{13}C NMR spectrum, the CH_2CH_3 side group in P(ETA) gave rise to two resonances with high intensity peaks at 14.6 and 23.2 ppm. The low-field chemical shift of the carbonyl resonance of the thioester (201.2 ppm) is in the expected range in which the carbonyl carbon resonance of aliphatic thioesters is found at 193–203 ppm.⁴² The main reason for employing P(ETA) rather than P(BuTA) is that the distinctive peaks for the side groups are relatively easy to compare by NMR spectroscopy. The purified polymer P7 was further used with different amines for a series of amidation reactions. The experiments were carried out with varying quantities of the amines employed relative to the thioester moiety in the polymer.

Initially, benzylamine was employed as a model amine, as it shows a distinct proton resonance in the low-field region of 1H NMR (Fig. 3). Additionally, parallel experiments were performed, in which every other reactant (*e.g.* base and thiol) was varied. In the first reaction, thiophenol was used as a catalyst to undergo a *trans*-thioesterification, followed by the amidation of thioesters.^{43–46} For this, the purified polymer was dissolved in dry THF and 2.50 equivalents of benzylamine were added to the mixture, followed by the addition of 2.00 equivalents of TEA and thiophenol (2.00 equivalents with respect to a single repeating unit of ETA). The mixture was stirred for 48 hours at room temperature and finally dialysed against THF/H₂O (9 : 1), concentrated and freeze dried to give the corresponding poly(ETA)-*r*-(benzyl acrylamide) P8. The com-

parison of the 1H NMR spectra of the starting polymer (P7) and the obtained polymer from the amidation reaction indicates that the amide bond is present in 22% of P8. It is important to note that the $-NH-CH_2$ -signal of the incorporated benzylamine was compared to the CH_2 -peak ETA to calculate the percentage of amine incorporation into the polymer. Following the substitution of P(ETA) with benzylamine, GPC traces show a shift to a higher molar mass value, which increases from 1300 g mol⁻¹ to 1500 g mol⁻¹. Visual appearance of the purified polymer has also changed significantly. While P(ETA) appears as a very sticky yellow gel, it becomes a pale yellow powder following substitution (P8, Fig. S13†).

In a second attempt, the amount of amine has been quadrupled to 10.0 equivalents and the reaction was followed by 1H NMR spectroscopy (Fig. S14†). The degree of amidation (DA) can be calculated by comparing the ratios of H_e and H_c (2 : 5) and was determined to be 28% in P9. Given a suitable higher reaction temperature of 50 °C, the amidation could be improved to higher yields of 44% for P10 (Fig. S15†). The temperature was further increased to 75 °C, when the reaction was carried out under microwave irradiation, as the heating can be easily controlled, which also allowed for a pressurised system at higher temperatures to be used. For this reaction (P11), a full substitution with benzylamine was achieved and verified by NMR analysis (Fig. 3C). In the 1H NMR spectrum of P11, no resonance for the SCH_2 group (H_c) of the side chain is detectable at 2.87 ppm after purification (Fig. 3C). Additionally, the monomer methyl group at 1.36 ppm (H_d) disappears as well, leaving only the resonances for the methyl

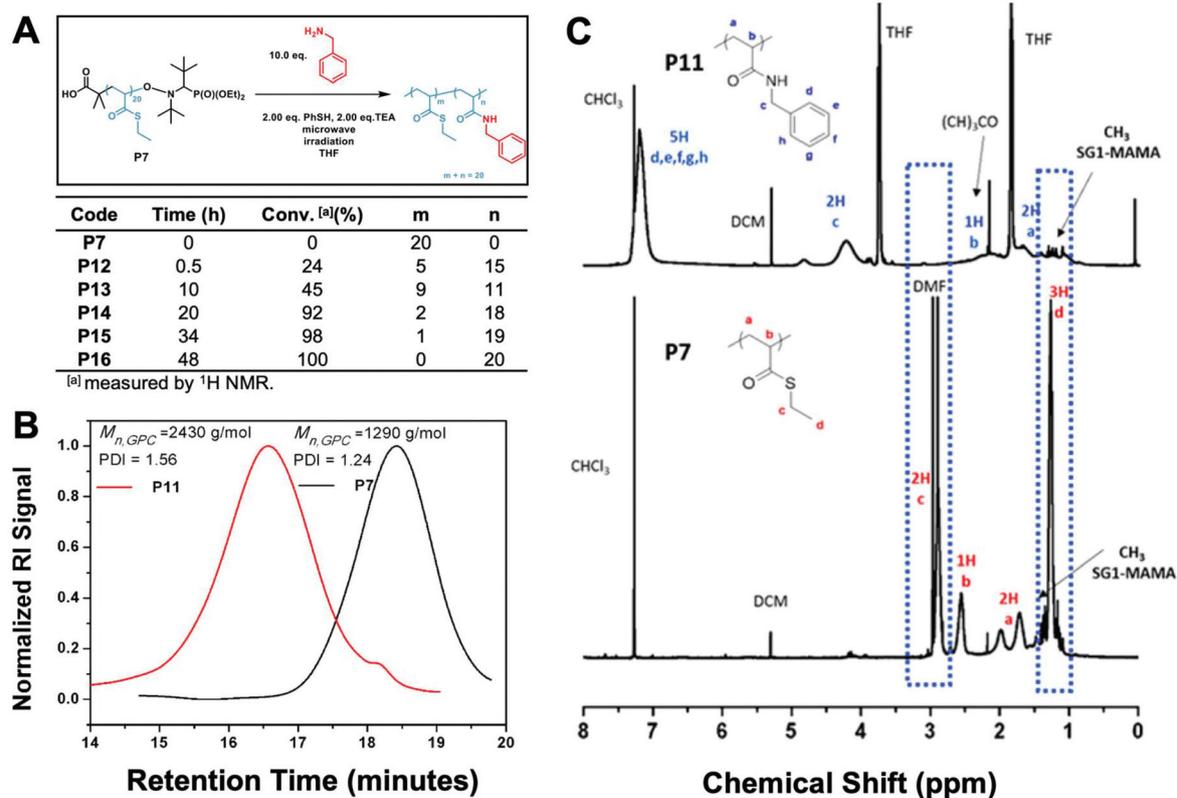


Fig. 3 (A) The reaction scheme for the amidation of P(ETA) (P7) with benzylamine and the reaction kinetics, (B) GPC traces of P(ETA) P7 and P(benzyl acrylamide) P11 and (C) the ¹H NMR spectrum of P7 and P11 recorded in CDCl₃.

group of SG1-MAMA visible. Furthermore, the transformation entails the formation of a new peak arising for NCH₂- (H_c), as well as a peak for the aromatic group (H_d-H_h). The GPC measurements following the full substitution of P(ETA) with benzylamine show a shift to high molecular weights (Fig. 3B), increasing from 1300 g mol⁻¹ to 2400 g mol⁻¹ (PDI = 1.56).

In another set of experiments, conditions used for full amidation in P11 were used to further investigate the amidation kinetics of P(ETA). For this, a microwave vial was charged with 100 mg of P(ETA) and THF, followed by the addition of [polymer]:[BzNH₂]:[PhSH]:[TEA] = 1:10:2:2. The vial was sealed with a rubber septum and the reaction mixture was stirred under the respective conditions for a designated period of time (0.5, 10, 20, 34, and 48 h) at 75 °C (Fig. 3A). It was found that after 20 hours, the amidation percentage reached 92%, while full amidation took 48 hours. The results obtained show that a range of amidation percentages can be targeted by reaction times.

It was then sought to generate a thermoresponsive polymer through the addition of *N*-isopropylamine using the amidation process (Fig. 4A). The amidation with *N*-isopropylamine resulted in successful substitution with full conversion according to the obtained ¹H NMR spectrum and resulted in an increase of molecular weight determined by GPC analysis (Fig. 4B-5C).

While $M_{n,GPC}$ increased from 1290 g mol⁻¹ to 1410 g mol⁻¹, the dispersity increased to a higher value of 1.48. It should be

noted that a much more evident increase had been observed when the amidation was previously carried out with benzylamine (compared with P11). This is likely due to a higher hydrodynamic volume observed for P11, whereas the difference between P7 and P17 is much smaller. While the conservation or the absence of the chain end could also influence the values at such short chain lengths, their influence could not be compared due to the overlap of the methyl signals for P17 and the SG1-MAMA end group in this study.

In the ¹H NMR spectrum for P17, no resonance for the SCH₂-group (H_c) of the side chain was detected, indicating full amidation. Additionally, the methyl group at 1.36 ppm disappeared (H_d) and a new peak for the two methyls of the isopropyl group at 1.16 ppm appeared. The proton from the tertiary carbon in H_e appeared as a new peak at 4.03 ppm, while the SCH₂-proton next to it disappeared. As for the polymers obtained by amidation with benzylamine, the sticky polymer P7 is obtained as a white powder after the amidation (Fig. S19[†]). The use of *N*-isopropylamine to carry out amidation on P(ETA) shows that the established protocol can be applied to various amines.

Transformation of poly(thioacrylate)s into poly(acrylate)s via an esterification reaction

It was sought to introduce functional alcohols capable of broadening the spectrum of the functionalisation of

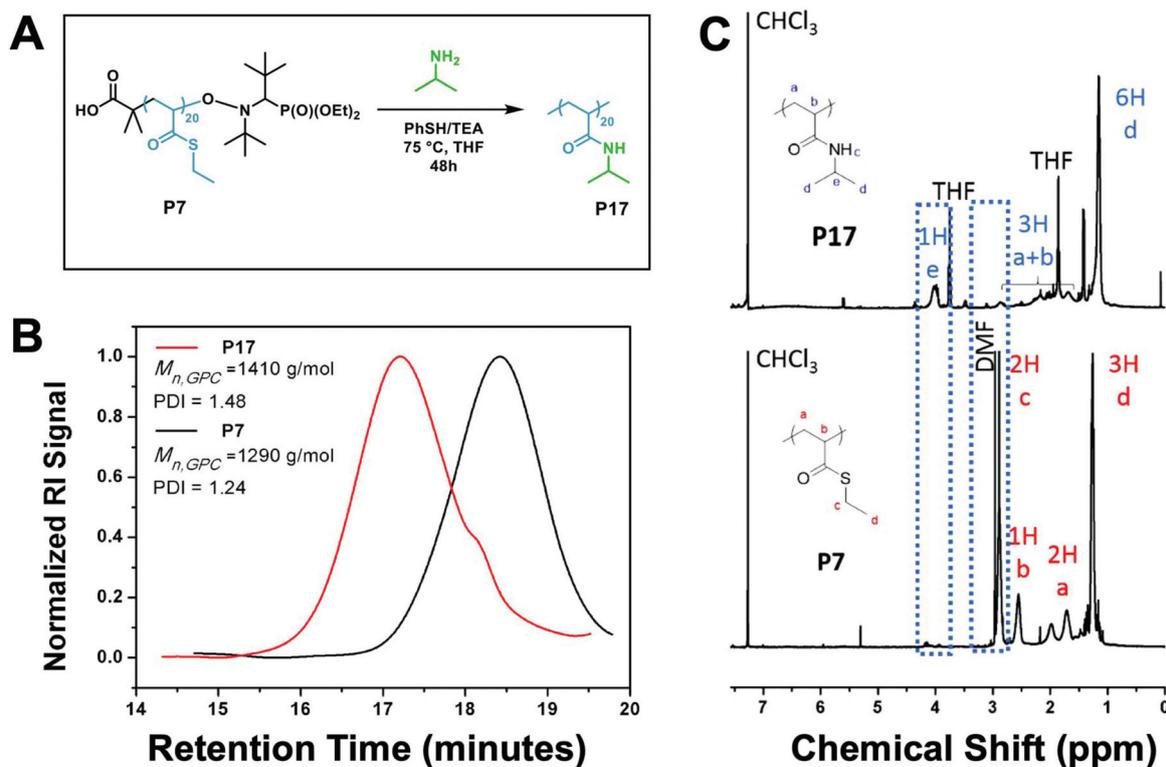


Fig. 4 (A) The reaction scheme for the amidation of P(ETA) (P7) with N-isopropylacrylamide (P17), (B) GPC traces of P(ETA) P7 and P(N-isopropylacrylamide) P17 and (C) the ^1H NMR spectrum of P7 and P17 recorded in CDCl_3 .

poly(thioacrylate)s. The resultant polymer, **P18**, containing an ester functionality was prepared *via* a post modification reaction with benzyl alcohol (Fig. 5A). In the ^1H NMR spectrum of the purified polymer **P18**, the resonance of the OCH_2 -group is visible at 5.12 ppm, which proves that an esterification reaction took place (Fig. 5B). Furthermore, a resonance at high frequencies can be identified based on the protons of the aromatic ring at 7.38 ppm. A second peak is, however, visible in close distance at 7.48 ppm, which was attributed to thiophenol. This observation can be explained by a competitive thiol–thioester exchange reaction, where the aromatic group shows that these protons are present in a 6:4 ratio, supporting the replacement with thiophenol, as well as with benzyl alcohol. From the comparison of the OCH_2 -group and the methyl group of SCH_2CH_3 from P(ETA), the presence of benzyl alcohol only along the polymer was calculated to be 18%.

Thermal properties of poly(ethyl thioacrylate)-*r*-(benzyl acrylamide) copolymers

A change in the properties of polymers, such as glass transition temperature (T_g), was characterised by performing differential scanning calorimetry (DSC) on the polymers obtained *via* post polymerisation modification with benzyl amide. To evaluate and verify the change in T_g , the obtained DSC chromatograms were analysed and compared to the representative DSC curves of the starting polymer (P7). The NMP of ETA

initiated by SG1-MAMA yielded a polythioacrylate with a glass transition temperature T_g of 32.2 °C. Benzyl acrylamide (BzAm) has been homopolymerised *via* RAFT (P19) and its T_g value of 61.8 °C was used as a value for comparison to study the progress of amidation on P(ETA). The polymers (P12–P16) from the amidation reactions on P7 show various BzAm contents with 24%, 45%, 92%, 98% and 100% calculated from the number of repeating units. The T_g value of P7 was increased by incorporating 24% of BzAm units (P(ETA)₁₅-*r*-BzAm₅) in the homopolymer to 4.4 °C (Fig. 6). In P14, 92% of BzAm were incorporated, yielding the copolymer P(ETA)₂-*r*-BzAm₁₈ with a T_g of 28.6 °C. The T_g values of all modified P(ETA)s have increased steadily with the increased incorporation of BzAm units in the polymer. The highest T_g value was recorded for P16 with 49.2 °C, where all thioester pendant groups were successfully transformed into amide groups. This result is also close to the value of P(BzAm) obtained *via* RAFT (T_g = 61.8 °C); however, it remains *ca.* 10 °C due to the presence of the trithiocarbonate end groups from the chain transfer agent for P19. Overall, it can be concluded that the amide moieties in the pendant group affect the physical and chemical properties when the structure changes to an acrylamide. From a polythioacrylate to its corresponding polyacrylamide, the T_g value changed by a total of 94 °C, which not only illustrates the ease of functionalization, but also proves that this is a versatile approach as a modern functionalization technique that can target various T_g values.

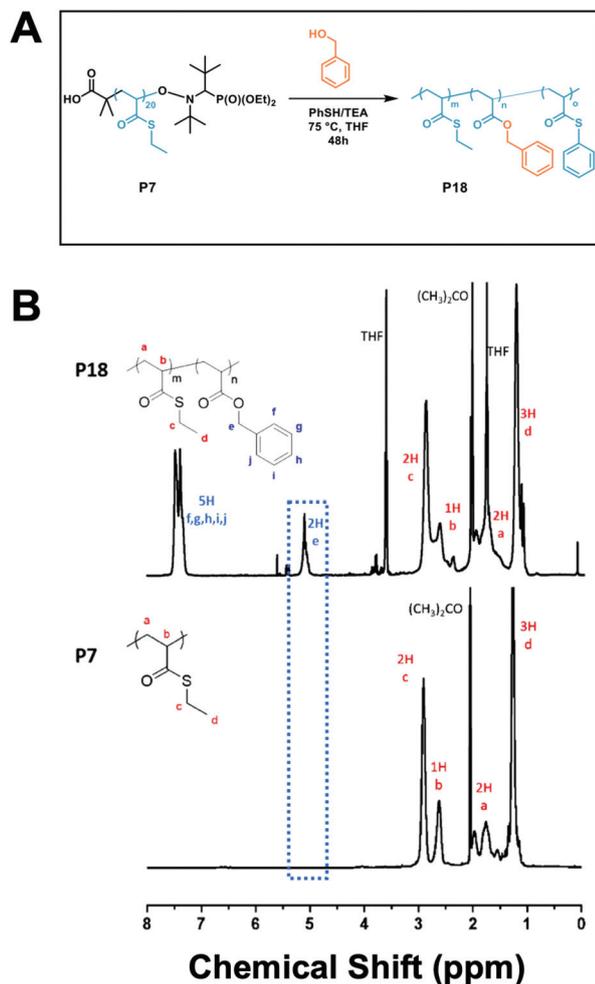


Fig. 5 (A) The reaction scheme for the partial esterification of P(ETA) (P7) with benzyl alcohol (P18) and (B) the ^1H NMR spectrum of P7 and P18 recorded in CDCl_3 .

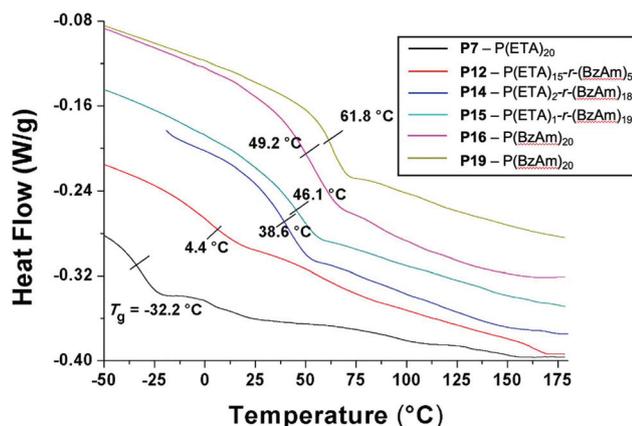


Fig. 6 DSC thermographs (Exo. up) for the second heating of a homopolymer of ETA (P7) and copolymers obtained by modification with benzylamine (P12, P14, P15 and P16) and a homopolymer of BzAm (P19) obtained by RAFT polymerisation as a reference.

Conclusions

In summary, NMP has been used for the polymerisation of thioacrylates with short hydrocarbon chains (ethyl and butyl) for the first time. Polymerisation of both alkyl-thioacrylates (ETA and BuTA) was carried out in DMF in a controlled manner with full monomer conversion and moderate dispersity values (<1.46) and was found to be much faster when compared to their acrylate counterparts. Furthermore, a comparison was made between the copolymerisation of thioacrylate and acrylate with PFS *via* kinetic sampling, which revealed that thioacrylates not only polymerised faster than acrylates, but also at the same time significantly enhanced the polymerisation rate of PFS, resulting in full conversion after 60 minutes, whereas the copolymerisation with acrylates only reached 10%.

Additionally, a simple modification approach that allows an overall transformation of poly(thioacrylate)s using thiophenol under microwave irradiation was investigated. This methodology proceeds under exceptionally mild reaction conditions and was found to allow functionalisation with amines and alcohols as nucleophiles. While full amidation was achieved with benzylamine and *N*-isopropylamine in P11 and P16, incomplete substitution was observed with benzyl alcohol in an esterification reaction in P18. However, this approach offers an efficient way to transform homopolymers into copolymers, by adding amines or alcohols of choice. Finally, with the help of DSC measurements on a series of partially amidated P(ETA)s, we have shown that poly(thioacrylate)s can be useful in delivering polymers with tunable physical, thermal and mechanical properties.

Author contributions

SA and RL have performed the synthesis and analysis. All authors have contributed to the design of the project and to writing the manuscript.

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Conflicts of interest

There are no conflicts to declare.

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