How to cite: *Angew. Chem. Int. Ed.* **2024**, *63*, e202317071
doi.org/10.1002/anie.202317071

Polymer Chemistry

RAFT Polymerisation by the Radical Decarboxylation of Carboxylic Acids**

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Abstract: The controlled grafting of polymers from small- and macro-molecular substrates is an essential process for many advanced polymer applications. This usually requires the pre-functionalisation of substrates with an appropriate functional group, such as a RAFT agent or ATRP initiator, which requires additional synthetic steps. In this paper, we describe the direct grafting of RAFT polymers from carboxylate containing small molecules and polymers *via* photochemical radical decarboxylation. This method utilises the innate functional groups present in the substrates, and achieves efficient polymer initiation in a single step with excellent control of molecular weight and dispersity.

Introduction

In the last 25 years, the introduction of controlled radical polymerisation methods, including reversible addition-fragmentation chain-transfer (RAFT)[1] and atom transfer radical polymerisation (ATRP),[2] has offered an unprecedented level of control over the dispersity and architecture of polymeric materials. These methods have been widely adopted in biomedical and materials science, with numerous commercial applications.[3] Many advanced applications of controlled polymerisation require the covalent linking of the polymer with small molecules (polymer functionalisation)[4] or other macromolecules (polymer grafting).[5]

Polymer grafting can be achieved by either attaching an existing polymer chain to a substrate ("grafting to") or by polymerising monomers from a reactive site present on the substrate ("grafting from"). "Grafting from" methods are often favored due to their ability to introduce dense functionalisation to a substrate.[6] In the case of RAFT and ATRP, this means that the macromolecular substrate must be chemically modified by attaching the RAFT agent or ATRP initiator prior to polymerisation (Figure 1A). While effective, this approach requires multistep synthesis which adds cost and complexity to the process and limits its commercial application.

In a more ideal approach, polymer grafting would be performed directly from a functional group already present in the starting material, leading to the formation of polymer conjugates *via* robust C–C bonds in a single functionalisation/polymerisation step. This method should utilise a common functional group that is naturally found in a wide range of small molecules and materials. Fors and co-workers

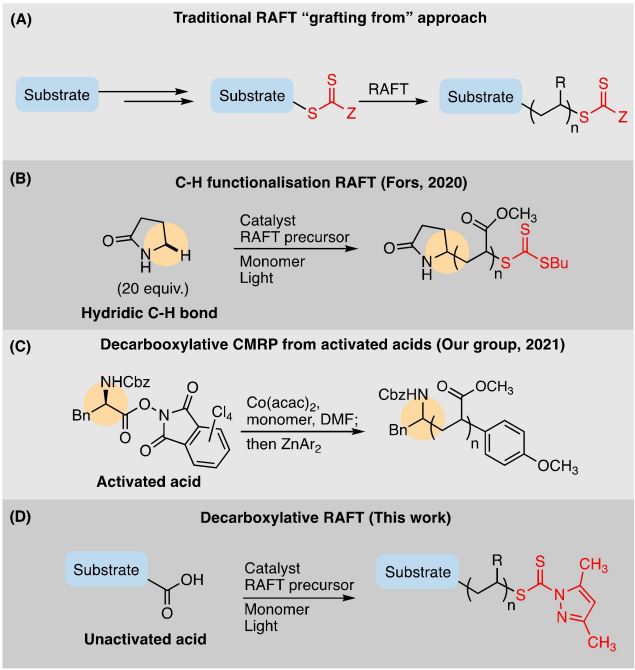

Figure 1. Approaches to polymer grafting. (A) Traditional multistep functionalisation/polymerisation; (B) C–H functionalisation RAFTS by Fors; (C) Decarboxylative CMRP (D) This work: decarboxylative RAFT.

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[**] A previous version of this manuscript has been deposited on a preprint server (https://doi.org/10.26434/chemrxiv-2023-w6lkp).

have recently reported controlled radical polymerisations from hydridic C–H bonds, using a hydrogen atom transfer (HAT) RAFT approach employing 20–116 equivalents of the C–H initiator (Figure 1B).[7]

One particularly attractive functional group for polymer grafting is the carboxylic acid, which is ubiquitous across biopolymers (polysaccharides, peptides, proteins etc.), synthetic polymers, medicinally relevant small-molecules, and natural products. An approach which allows for the controlled grafting of polymers from carboxylic acids could enable the direct synthesis of polymer conjugates of all these materials, leading to a wealth of opportunities for new polymer conjugates and polymer architectures.

In 2021, our group reported the cobalt-mediated radical polymerisation (CMRP) of acrylates and acrylamides initiated by the radical decarboxylation of activated carboxylic acids (Figure 1C).[8] This method allows for the synthesis of polymer conjugates from peptides and other highly functional materials with excellent control of the polymer molecular weight and dispersity. The main disadvantage of this method is that it requires the conversion of carboxylic acids to tetrachlorophthalimide esters ("activated acids") prior to the polymerisation reaction. We have also reported the uncontrolled grafting of polymers from carboxylic acid groups on oxidised nanocellulose, using a silver-promoted radical decarboxylation to initiate polymerisation.[9]

In this paper, we report the synthesis of RAFT polymers via the photochemical radical decarboxylation of unactivated carboxylic acids (Figure 1D). This method proceeds in a single step, using one equivalent of carboxylic acid substrate and delivers polymers with good control of molecular weight and dispersity.

The radical decarboxylation of carboxylic acids has been widely adopted in the small-molecule catalysis community for the formation of carbon-carbon bonds.[10] Much of this work has been driven by recent advances in photoredox catalysis, which has enabled redox-neutral cross-coupling reactions of carboxylic acids with a variety of partners.[11] In 2014, MacMillan and co-workers reported the decarboxylative coupling of carboxylic acids with acrylates and other Michael acceptors.[12] In these reactions, the photocatalyst (PC) facilitates a single-electron oxidation of the carboxylate to achieve the decarboxylation, resulting in a radical that adds to the acrylate acceptor. The reduced form of the catalyst ($PC^{\bullet\ominus}$) then reduces the product radical in a radical termination step.

Radical decarboxylation has been used to initiate radical polymerisations, albeit in an uncontrolled manner. In 2017, Ni and co-workers demonstrated the use of TiO_2 nanoparticles and UV light to polymerise vinyl acetate *via* the decarboxylation of diacids.[13] In the same year, Sugihara and Yoshimi reported the polymerisation of acrylate and acrylamide monomers *via* radical decarboxylation, using a system of dual stoichiometric organic photosensitisers and UV light.[14] In both of these reports, turnover of the photocatalyst/photosensitiser was proposed to reduce the propagating polymer radical, leading to a hydrogen atom at the ω-end of the polymer after protonation of the anion. Decarboxylative coupling reactions have also been successfully used for the post-polymerisation functionalisation of polymers, from both free carboxylic acids[15] and activated esters.[16]

In order to apply a catalytic decarboxylation strategy to controlled radical polymerisations, reduction of the carbon-centered radical by the photocatalyst must be avoided. We hypothesised that this might be achieved with the use of a sacrificial oxidant. In our proposed reaction design, this sacrificial oxidant is a thiocarbonyl radical, formed by the addition of a carbon-centered radical to a thiocarbonyl disulfide compound (Figure 2). This will result in quenching the reduced form of the photocatalyst, allowing for catalyst turnover, while also forming a RAFT agent in situ.

In 1982, Otsu and co-workers reported the use of thiuram disulfides and xanthate disulfides as photoiniferters for controlled radical polymerisations.[17] More recently, the groups of Müllner[18] and Perrier[19] have shown that thiocarbonyl disulfides can act as photoiniferters under photocatalytic or catalyst-free conditions. Thiocarbonyl disulfides have also been used extensively as precursors for the synthesis of RAFT agents,[20] and for the in situ conversion of atom transfer radical polymerisation (ATRP) initiators into RAFT mediators.[21]

Results and Discussion

We began our study by examining the polymerisation of methyl acrylate (MA), initiated by the decarboxylation of benzyl chloroformate (Cbz) protected phenylalanine (**1**) in the presence of a photocatalyst, the RAFT precursor **4** and green or blue light (Table 1). We examined several acridinium based organocatalysts (**PC1-3**), due to their known efficacy in radical decarboxylations.[22] The catalysts **PC1-3** have excited state reduction potentials of 2.06, 2.08 and 1.68 V respectively (vs SCE), and excited state lifetimes of 6.4, 14.4 and 12.3 ns.[22] Of these catalysts, **PC3** was the most effective, showing 99 % monomer conversion after overnight irradiation (Table 1, entry 3). The success of this catalyst is likely due to its significantly improved photostability, compared with **PC1** and **2**.[22] GPC analysis of this polymer showed a low dispersity (1.19) and an $M_{n\ (GPC)}$ of 15,800 g/mol. This is in good correlation with the $M_{n\ (NMR)}$ (12,000 g/mol) calculated by integration of the NMR signal associated

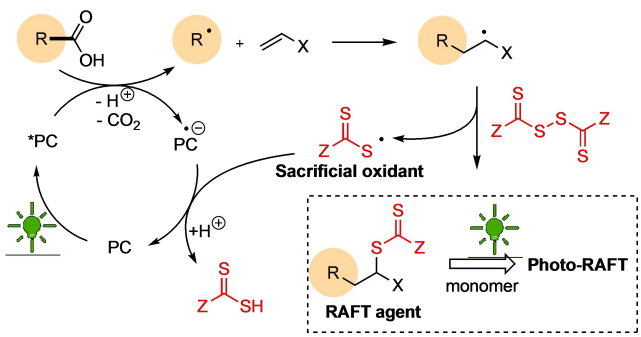
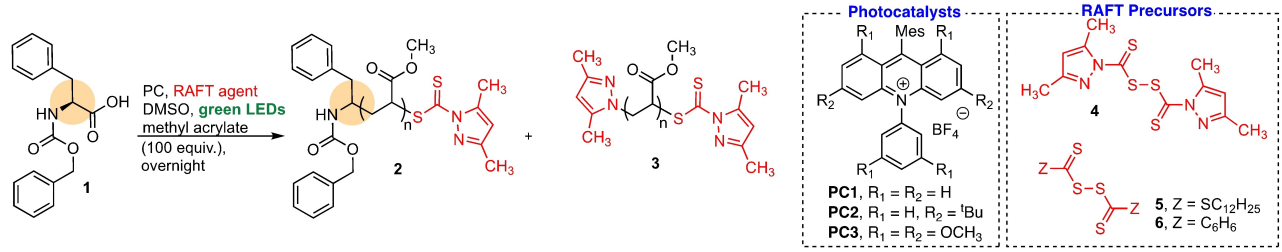


Figure 2. Reaction design for decarboxylative RAFT.

Table 1: Optimisation of the decarboxylative photo RAFT polymerisation.



Entry	1 : RAFT : PC	RAFT	PC	Light source	Conv. (%)[a]	Mn (theory)	Mn (NMR)[b]	Mn (GPC)[c]	Đ	Ratio 2 : 3[d]
1	1 : 1 : 0.05	4	PC1	Green LEDs	0	–	–	–	–	–
2	1 : 1 : 0.05	4	PC2	Green LEDs	0	–	–	–	–	–
3	1 : 1 : 0.05	4	PC2	Blue LEDs	97%	8800	21,600	19,200	1.31	65 : 35
4	1 : 1 : 0.05	4	PC3	Green LEDs	99%	8900	12,000	15,800	1.19	90 : 10
5	1 : 1 : 0.05	4	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	Blues LEDs	84%	8000	18,400	17,900	1.45	65 : 35
6	1 : 1 : 0	4	–	Green LEDs	0	–	–	–	–	–
7	1 : 1 : 0.05	4	PC3	None	0	–	–	–	–	–
8	0 : 0 : 0.05	–	PC3	Green LEDs	18	–	–	20,900	2.1	–
9	1 : 0.5 : 0.05	4	PC3	Green LEDs	97	8800	17,000	27,200	1.27	95 : 5
10[e]	1 : 1 : 0.01	4	PC3	Green LEDs	97	8800	20,000	18,000	1.14	70 : 30
11[e]	1 : 1 : 0.05	5	PC3	Green LEDs	66	6000	65,000	15,000	1.14	–
12[e]	1 : 1 : 0.05	6	PC3	Green LEDs	0	–	–	–	–	–

Mn in g/mol; [a] Determined by ^{1}H NMR analysis of crude product; [b] Determined by NMR analysis of precipitated polymer; [c] Determined by GPC analysis of precipitated polymer; [d] Determined by ^{1}H NMR analysis, [e] Performed with [MA] = 6.52 M.

with the α-endgroup (derived from **1**) and the bulk polymer. This indicates that a high level of desired endgroup incorporation was achieved.

Analysis of this material by ^{1}H NMR and ESI-MS (see below) showed the presence of a second polymer species **3**, incorporating a dimethyl pyrazole heterocycle at the α-endgroup. Integration of the ^{1}H NMR showed a 90 : 10 ratio of the desired polymer **2** (determined by integration of the aromatic α-endgroup) to the byproduct **3** (determined by integration of the pyrazole α-endgroup proton at δ 5.73 ppm).

In contrast to the success of acridinium catalyst **PC3**, the use of the iridium-based catalyst $(Ir[dF(CF_3)ppy]_2$-$(dtbpy))PF_6$ gave good conversion, but increased dispersity and reduced incorporation of the desired endgroup (Table 1, entry 5).

In control experiments, no polymerisation was observed in the absence of photocatalyst or in the dark (entries 6–7), while the absence of **1** and **2** resulted in low monomer conversion (18 %) and high dispersity (entry 8). Reducing the amount of RAFT precursor (**4**) from 1 to 0.5 equivalents led to a 95 : 5 ratio of polymers **2** and **3**, but an increase in the M_n and dispersity of the resulting polymer (entry 9). This is consistent with our proposed mechanism (Figure 2) where half of the thiocabonylthio disulfide is consumed as a sacrificial oxidant, requiring the use of a full equivalent of this reagent.

The catalyst loading was reduced to 1 % (entry 10) which showed a lower degree of endgroup incorporation compared with 5 % catalyst loading.

Alternative RAFT precursors were also trialed, with the trithiocarbonate disulfide **5** giving reduced monomer conversion and endgroup incorporation, while the phenyl dithiocarbonate disulfide **6** gave no polymer product (entries 11–12).

Proton NMR analysis of the polymer from our optimised conditions (Table 1, Entry 4) showed the presence of aromatic and benzylic protons, consistent with good incorporation of the α-endgroup derived from **1** (Figure 3). In addition, the pyrazole proton could also be observed at δ 6.34 ppm, consistent with incorporation of the RAFT agent at the ω-end. Integration of these signals showed a 1 : 0.7 ratio between the α-endgroup and the RAFT agent, indicating a good level of ω-endgroup fidelity.

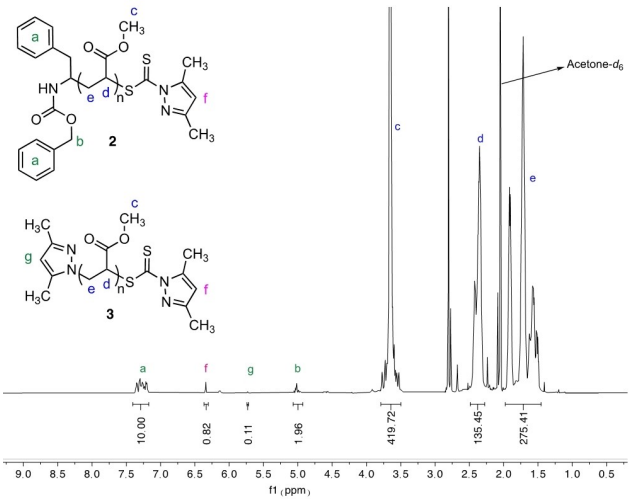


Figure 3. ^{1}H NMR spectra of polymer 2 (Table 1, entry 4).

DOSY NMR analysis was used to confirm incorporation of the desired endgroups (See SI, Figure S47). The diffusion coefficients associated with the aromatic NMR signal and the RAFT derived signal were 2.41×10^{-10} and $2.12\times10^{-10}\,m^2s^{-1}$ respectively, compared with $2.09\times10^{-10}\,m^2s^{-1}$ for the signals associated with the polymer backbone and $2.43\times10^{-9}\,m^2s^{-1}$ for the solvent. This indicates that the endgroup NMR signals in polymer **2** are diffusing at a similar rate to the polymer and are not associated with small molecule impurities.

Electrospray ionisation mass spectrometry (ESI-MS) was used to analyse polymer **2** at low monomer conversion (32 % conversion). The MS spectra (Figure S49**)** shows two main species: the first consistent with polymer **2** with the desired α- and ω-endgroups (1480.5538 calcd. for n = 12, found 1480.5561, $[M+Na]^+$) and the second consistent with polymer **3** containing a pyrazole group at the α-end and a thiocarbonylthio moiety at ω-end (1493.5702 calcd. for n = 14, found 1493.5704, $[M+Na]^+$).

Kinetic analysis of the polymerisation reaction showed an initial induction period of around 4 hours, followed by a linear dependance of $\ln([M]_0/[M]_t)$ versus time, with an observed increase in the reaction rate after 10 hours. This trend can be attributed to an increase in the concentration of propagating radicals over the course of the reaction, as the decarboxylation of **1** initiates more polymer chains. Additional kinetic experiments showed a reduction in the induction period to 2 hours when 10 mol % photocatalyst was used, and an even further decrease when a blue LED lamp was used instead of green light (Figure S50). Increased catalyst loading and the use of blue light, however, did not result in improved endgroup incorporation compared with the standard conditions.

We observed a linear increase in molecular weight of the polymer with increasing monomer conversion (Figure 4B) and a consistent dispersity of 1.1–1.2.

These data indicate that this method shows the characteristics of living polymerisation, where irreversible chain termination is not significant. We also examined the temporal control of this reaction through an "On/Off" experiment (Figure 4C) by switching the light source off and on after an initial induction period of 8 hours. We observed no polymerisation during the "off" periods, confirming that this polymerisation is following a photo-RAFT mechanism, rather than photochemical initiation followed by a traditional RAFT mechanism *via* degenerative chain transfer.

The living nature of this photoRAFT polymerisation was also tested by chain extension experiments to confirm the fidelity of the RAFT endgroup. Polymer **2** ($Mn_{(GPC)}$ = 16,600 g/mol; $Đ$ = 1.15) was used as a macro initiator and was treated with 500 equivalents of methyl acrylate under green light irradiation overnight (Figure 5A). This resulted in 88 % monomer conversion, and the isolation of a chain extended poly(methyl acrylate) ($Mn_{(GPC)}$ = 51,800 g/mol; $Đ$ = 1.41). Additional chain extensions were also successfully conducted with dimethylacrylamide ($Mn_{(GPC)}$ = 69,100 g/mol; $Đ$ = 1.46), while chain extension with methyl methacrylate gave a less controlled polymerisation ($Mn_{(GPC)}$ = 46,900 g/mol; $Đ$ = 2.2).

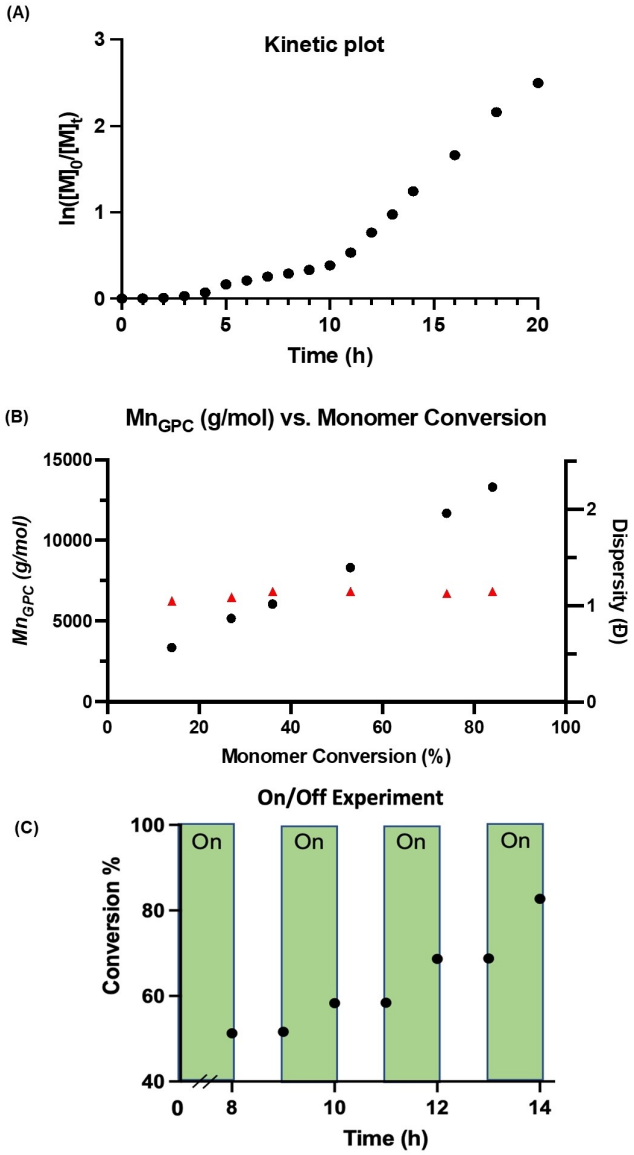


Figure 4. Kinetic experiments; (A) Monomer conversion vs time; (B) Mn (GPC) and dispersity vs time; (C) On/off experiment.

As these chain extension experiments were conducted in the absence of the photocatalyst, this suggests that the role of the catalyst is limited to promoting radical decarboxylation only, and is not required for the subsequent polymerisation. This was tested by conducting photoRAFT polymerisations of the commercially available RAFT agent **8** in the presence and absence of photocatalyst **PC3** (Figure 5B). Both reactions proceeded well under green light irradiation, with the photocatalyst increasing the monomer conversion by only 10 % after 16 hrs. This shows that **PC3** has only a minimal influence on the rate of polymerisation under these conditions.

This suggests that the polymerisation under photochemical conditions is primary driven by the direct photolysis of the C–S bond by green light, as reported by Boyer[24] and others. The slightly increased conversion in the presence of

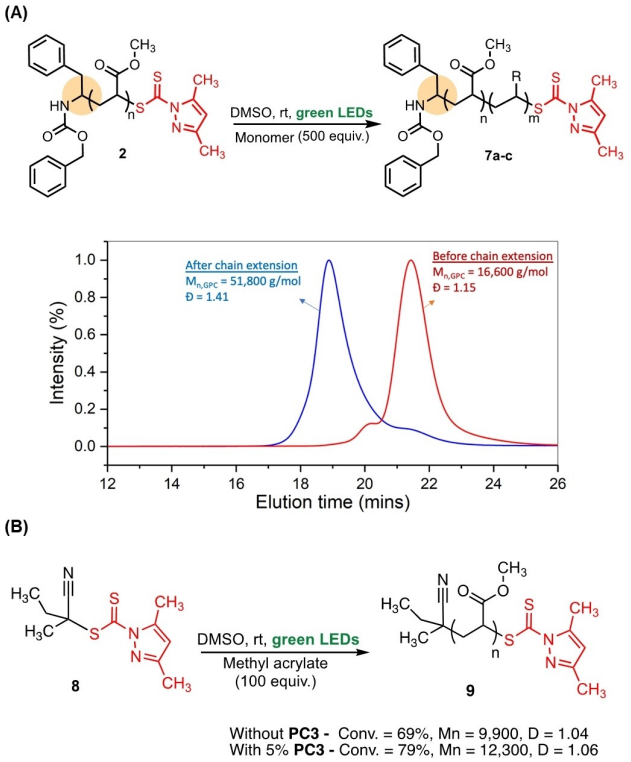


Figure 5. (A) Chain extension experiment of polymer 2. (B) Effect of photocatalyst on RAFT polymerisation with RAFT agent 8.

PC3 may suggest that a photoinduced electron/energy transfer (PET) RAFT mechanism is also competitive under these conditions, likely to occur *via* an energy transfer rather than an electron transfer due to the oxidising nature of the photocatalyst.

In order to explain the formation of polymer **3** under our reaction conditions, we undertook some small-molecule experiments with the RAFT precursor **4** and a single equivalent of butyl acrylate (Figure 6). After irradiation with green light for 18 hours in DMSO, the β-dithiolactone **11** and the pyrazole dithiolate adduct **10** were isolated. We hypothesised that **10** may act as a photoiniferter for the formation of polymer **3**, however, the addition of 100 equiv. of MA and irradiation with green light did not lead to any polymerisation.

These experiments suggest that the RAFT precursor **4** can react with acrylate monomer in the absence of carboxylic acid or photocatalyst to give a nitrogen centered pyrazole radical leading to the formation of polymer **3**. However, once this pyrazole radical reacts with a thiol radical to generate **10**, this product is not photochemically active. A detailed mechanistic proposal for this pathway is given in the Supporting Information (Figure S51).

To further understand the decarboxylation step in our RAFT process, we performed a series of small molecule decarboxylative cross-couplings between carboxylic acids and the RAFT disulfide **4** in the absence of monomer (Figure 7). When the amino acid **1** was employed, consumption of the starting materials was observed, but the expected adduct **12** was not isolated. We suggest that this may be due to the instability of adduct **12** under the photochemical conditions. However, reaction of the benzylic carboxylic acid **1f** gave the RAFT agent **13** in 43 % isolated yield (55 % NMR yield). While a desmethyl analogue of **13** has been previously reported by Moad and co-workers as an active RAFT agent using a thermal initiator,[25] subjecting **13** to green light in the presence of 100 equiv. of methyl acrylate did not lead to polymer formation. This suggests that the benzylic C–S bond in **13** is not photolabile under these conditions, and that **13** is not a reactive intermediate in the synthesis of polymer **2f** (see Fig 8). This hypothesis was further supported when we attempted our standard decarboxylative polymerisation of **1** using styrene as monomer, leading to no observable polymer.

In contrast to previously reported decarboxylative couplings using acridinium photocatalysts, the addition of base was detrimental to the formation of **13**. A similar result was seen in our polymerisation reactions, suggesting that the reagent **4** may be incompatible with basic conditions.

The scope of the decarboxylative RAFT polymerisation was tested by examining a range of different initiating carboxylic acids (Figure 8). Amino acid derived substrates performed well in this reaction (**2a–c**) giving high monomer conversions and low dispersities (1.19–1.21). ^{1}H NMR

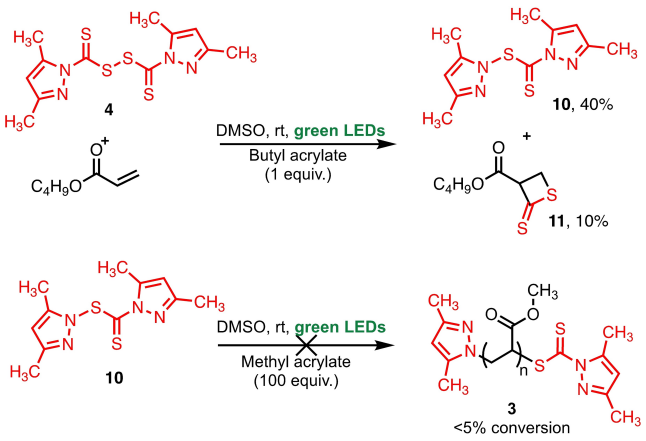


Figure 6. Mechanistic studies on the formation of polymer **3**.

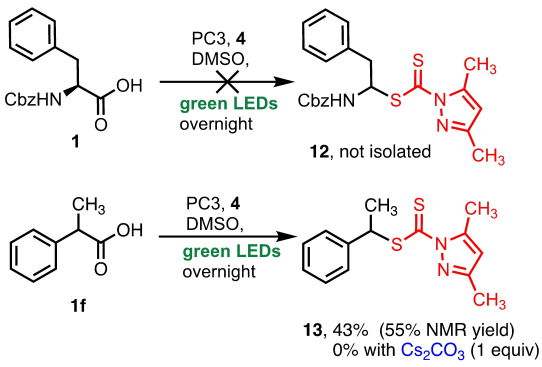


Figure 7. Decarboxylative thiolation in the absence of monomer.

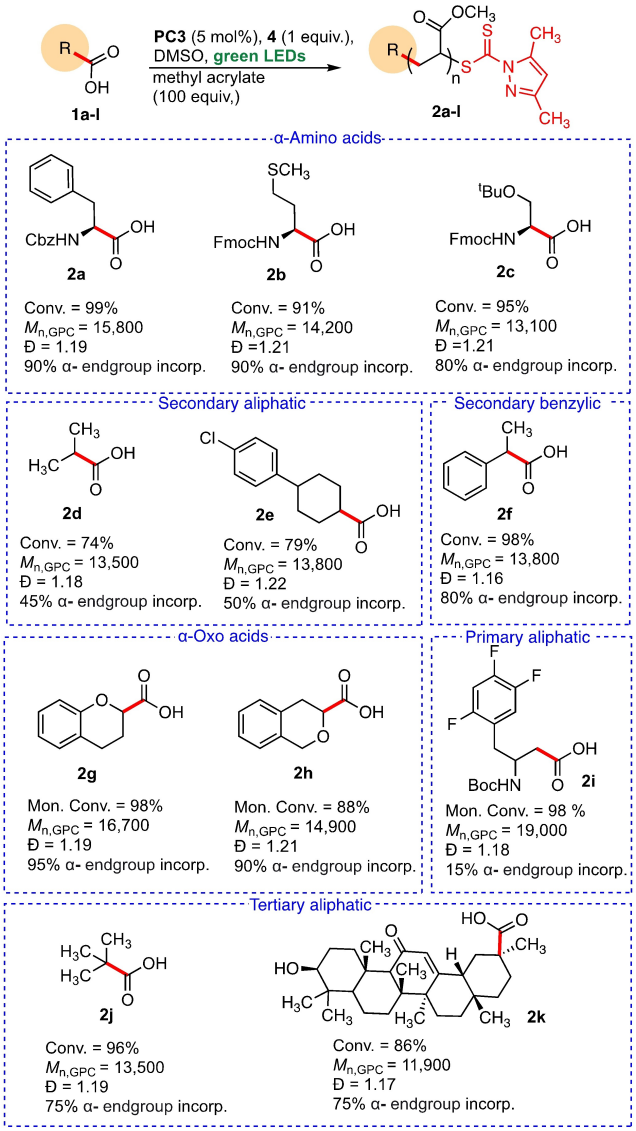


Figure 8. Scope of carboxylic acids in decarboxylative polymerisation and decarboxylative thiolation.

analysis showed 80–90 % incorporation of the desired α-endgroup, with the remainder consisting of polymer **3**. Secondary aliphatic carboxylic acids (**2d**,**e**) were less effective, giving lower monomer conversion (74–79 %) along with reduced incorporation of the α-endgroup (45–50 %). Secondary benzylic (**2f**) or α-oxo acids (**2g**,**h**) were excellent substrates for this reaction giving high levels of endgroup incorporation (80–95 %). The efficiency of carboxylic acid **2f** in this polymerisation is consistent with the small molecule results in Figure 7. An initiation efficiency (f) for **2f** of 50 % is observed, where $f = \mathrm{Mn_{theory}}/(\mathrm{Mn_{(GPC)}} \times \alpha\text{-endgroup incorp.})$, which is consistent with the 55 % NMR yield for the adduct **11**.

The primary carboxylic acid (**2i**), however, was less effective, with only 15 % incorporation of this molecule into the polymer. Finally, tertiary carboxylic acids were also tested (**2j**,**k**), showing 75 % incorporation of the desired α-endgroup into the polymer.

These results show that the effective incorporation of the carboxylate-derived functional group into the polymer is largely determined by the stability of the radical that is produced following decarboxylation. This is consistent with previous studies in decarboxylative cross coupling, where the highest yields are usually obtained with α-amino, α-oxo or benzylic carboxylic acids where the resulting radical is resonance stabilised. Similarly, tertiary radicals are well tolerated in our reaction, with secondary radicals showing moderate incorporation and primary radicals performing poorly, which correlates with the increased stabilisation of more substituted radicals by hyperconjugation. In addition, excellent functional group tolerance has been demonstrated, with redox sensitive functional groups such as thioethers and aryl halides well tolerated (**2b**,**e**), along with a free alcohol (**2k**).

We next looked to use our decarboxylative RAFT method for the synthesis of brush polymers (Figure 9). We used the random RAFT copolymer **14** as the backbone, containing a 5:1 ratio of methyl methacrylate and a carboxylic acid-containing monomer ($Mn_{(GPC)} = 25{,}000$ g/mol; $Đ = 1.19$). Following decarboxylative polymerisation and filtration, NMR analysis of the filtrate showed ≈20 % ungrafted polymer **3**, with the remaining polymer presumed to be grafted to form the brush polymer **15**. GPC analysis of the crude polymer shows a peak at 22 mins consistent with the ungrafted polymer ($Mn_{(GPC)} = 22{,}300$ g/mol; $Đ = 1.26$) along with a bimodal peak at 16 and 18 mins, consistent with grafted polymer. Precipitation of this material selectively produced the higher molecular weight brush polymer. Analysis of polymers **14** and **15**

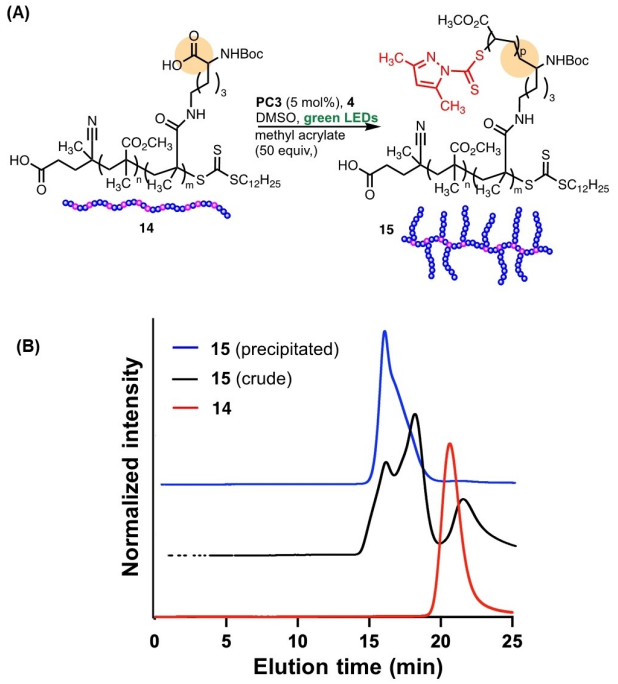
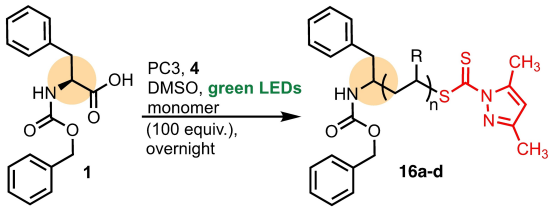


Figure 9. (A) Synthesis of brush polymer 13; (B) GPC traces of 12 (red, bottom), 13 crude (black, middle) and 13 precipitated (blue, bottom).

Table 2: Alternative monomers in decarboxylative RAFT.



Monomer	Conv. (%)[a]	Mn (NMR)	Mn[b] (GPC)	$Đ$[b]	Endgroup incorp.
BA	75	14,400	7,500	1.12	95%
MMA	99	32,300	26,500	1.56	75%
DMA	87	12,900	23,900	1.49	55%
NIPAM	89	33,200	38,100	1.58	80%

BA = butyl acrylate, MMA = methyl methacrylate, DMA = N,N-dimethyl acrylamide, NIPAM = N-isopropyl acrylamide, Mn in g/mol; [a] Determined by ^{1}H NMR analysis; [b] Determined by GPC analysis of precipitated polymer.

(precipitated) by dynamic light scattering (DLS) showed an effective diameter of 12 nm for **14** and 110 nm for **15**, with polydispersities of 0.2 and 0.3 respectively, consistent with successful brush synthesis. In addition, DOSY NMR analysis of this material showed matching rates of diffusion between the polymer backbone and the grafted arms, consistent with successful grafting (Figure S47).

Finally, we examined the compatibility of this reaction with alternative monomers in the decarboxylative polymerisation initiated by **1** (Table 2). Butyl acrylate (BA) showed lower conversion than MA after reaction overnight, but gave excellent dispersity and α-endgroup incorporation. Methyl methacrylate (MMA) gave a higher molecule weight polymer, with 75 % α-endgroup incorporation and moderate dispersity. Similarly, *N,N*-dimethyl acrylamide (DMA) gave modest endgroup incorporation and dispersity. *N*-isopropyl acrylamide (NIPAM) gave the best α-endgroup incorporation, with >95 % observed by ^{1}H NMR analysis.

Conclusion

In conclusion, we have demonstrated the first example of radical decarboxylation of carboxylic acids for the initiation of controlled radical polymerisations. This method utilises an organic photocatalyst, a commercially available RAFT precursor and green light to deliver polymers with excellent monomer conversion, dispersity and endgroup incorporation. Crucially, this is a one-step process that utilises innate carboxylate groups in the substrates, eliminating the need for multistep fuctionalisation/polymerisation processes.

A variety of carboxylic acids have been demonstrated, including carboxylate-containing synthetic and biopolymers, demonstrating the versatility of this method. We have shown that this method enables the direct synthesis of highly functionalised materials, and we believe it will simplify the synthesis of a range of polymer materials and complex polymer architectures.

Supporting Information

Experimental procedures, ^{1}H, ^{13}C and DOSY NMR spectra, GPC traces, ESI-MS and DLS data are available in the Supporting Information.

Abbreviations

RAFT Reversible addition-fragmentation chain-transfer,
ATRP Atom transfer radical polymerisation.

Acknowledgements

Open Access publishing facilitated by Monash University, as part of the Wiley - Monash University agreement via the Council of Australian University Librarians.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Decarboxylative Coupling · Photo Polymerization · Polymer Grafting

[1] a) J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, S. H., *Macromolecules* **1998**, *31*, 5559–5562; b) S. Perrier, *Macromolecules* **2017**, *50*, 7433–7447.

[2] J.-S. Wang, K. Matyjaszewski, *J. Am. Chem. Soc.* **1995**, *117*, 5614–5615.
[3] G. Moad, An Industrial History of RAFT Polymerisation. In *RAFT Polymerisation: Methods, Synthesis and Applications*, Vol. 2; Wiley, 2021.
[4] E. Blasco, M. B. Sims, A. S. Goldmann, B. S. Sumerlin, C. Barner-Kowollik, *Macromolecules* **2017**, *50*, 5215–5252.
[5] M. Á. Vega-Hernández, G. S. Cano-Díaz, E. Vivaldo-Lima, A. Rosas-Aburto, M. G. Hernández-Luna, A. Martinez, J. Palacios-Alquisira, Y. Mohammadi, A. Penlidis, *Processes* **2021**, *9*, 375.
[6] K. L. Beers, S. G. Gaynor, K. Matyjaszewski, S. S. Sheiko, M. Möller, *Macromolecules* **1998**, *31*, 9413–9415.
[7] E. E. Stache, V. Kottisch, B. P. Fors, *J. Am. Chem. Soc.* **2020**, *142*, 4581–4585.
[8] M. Ayurini, P. G. Chandler, P. D. O'Leary, R. Wang, D. Rudd, K. D. Milewska, L. R. Malins, A. M. Buckle, J. F. Hooper, *JACS Au.* **2022**, *2*, 169–177.
[9] a) D. J. Mendoza, M. Ayurini, C. Browne, V. S. Raghuwanshi, G. P. Simon, J. F. Hooper, G. Garnier, *Biomacromolecules* **2022**, *23*, 1610–1621; b) D. J. Mendoza, M. Ayurini, V. S. Raghuwanshi, G. P. Simon, J. F. Hooper, G. Garnier, *Macromolecules* **2023**, *56*, 3497–3506; c) V. S. Raghuwanshi, D. J. Mendoza, C. Browne, M. Ayurini, G. Gervinskas, J. F. Hooper, G. P. Simon, G. Garnier, *J. Colloid Interface Sci.* **2023**, *652*, 1609–1619.
[10] a) M. O. Konev, E. R. Jarvo, *Angew. Chem. Int. Ed.* **2016**, *55*, 11340–11342; b) N. Rodriguez, L. J. Goossen, *Chem. Soc. Rev.* **2011**, *40*, 5030–5048; c) F. Sandfort, M. J. O'Neill, Cornella, L. Wimmer, P. S. Baran, *Angew. Chem. Int. Ed.* **2017**, *56*, 3319–3323.
[11] Y. Jin, H. Fu, *Asian J. Org. Chem.* **2016**, *6*, 368–385.
[12] L. Chu, C. Ohta, Z. Zuo, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2014**, *136*, 10886–10889.
[13] W. Liao, X. Ni, *Photochem. Photobiol. Sci.* **2017**, *16*, 1211–1219.
[14] M. Yamawaki, A. Ukai, Y. Kamiya, S. Sugihara, M. Sakai, Y. Yoshimi, *ACS Macro Lett.* **2017**, *6*, 381–385.
[15] a) J. B. Garrison, R. W. Hughes, J. B. Young, B. S. Sumerlin, *Polym. Chem.* **2022**, *13*, 982–988; b) A. Adili, A. B. Korpusik, D. Seidel, B. S. Sumerlin, *Angew. Chem. Int. Ed.* **2022**, *61*, e202209085.
[16] a) S. Frech, P. Theato, *ACS Macro Lett.* **2022**, *11*, 161–165; b) S. Frech, E. Molle, A. J. Butzelaar, P. Theato, *Macromolecules* **2021**, *54*, 9937–9946; c) R. Chapman, D. Melodia, J.-B. Qu, M. H. Stenzel, *Polym. Chem.* **2017**, *8*, 6636–6643; d) J. B. Garrison, R. W. Hughes, B. S. Sumerlin, *ACS Macro Lett.* **2022**, *11*, 441–446.
[17] a) T. Otsu, M. Yoshida, A. Kuriyama, *Polym. Bull.* **1982**, *7*, 45–50; b) T. Otsu, *Polym. Chem.* **2000**, *38*, 2121–2136.
[18] K. Hakobyan, C. S. P. McErlean, M. Müllner, *Macromolecules* **2021**, *54*, 7732–7742.
[19] A. Kerr, G. Moriceau, M. A. Przybyla, T. Smith, S. Perrier, *Macromolecules* **2021**, *54*, 6649–6661.
[20] J. Chiefari, R. T. A. Mayadunne, C. L. Moad, G. Moad, E. Rizzardo, A. Postma, M. A. Skidmore, S. H. Thang, *Macromolecules* **2003**, *36*, 2273–2283.
[21] a) K. Hakobyan, C. S. P. McErlean, M. Müllner, *Macromolecules* **2020**, *53*, 10357–10365; b) C. M. Wager, D. M. Haddleton, S. A. F. Bon, *Eur. Polym. J.* **2004**, *40*, 641–645.
[22] A. Joshi-Pangu, F. Lévesque, H. G. Roth, S. F. Oliver, L.-C. Campeau, D. Nicewicz, D. A. DiRocco, *J. Org. Chem.* **2016**, *81*, 7244–7249.
[23] D. Roy, J. T. Guthrie, S. Perrier, *Macromolecules* **2005**, *38*, 10363–10372.
[24] J. Xu, S. Shanmugam, N. A. Corrigan, C. Boyer, *ACS Symp. Ser.* **2015**, *13*, 247–267.
[25] J. Gardiner, I. Martinez-Botella, J. Tsanaktsidis, G. Moad, *Polym. Chem.* **2016**, *7*, 481–492.

Manuscript received: November 9, 2023
Accepted manuscript online: November 21, 2023
Version of record online: December 20, 2023