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(2020)

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Polymer Chemistry, 11(40), pp. 6435-6440.

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<https://doi.org/10.1039/d0py01119c>

COMMUNICATION

Visible-Light Reversible Photopolymerisation: Insights via Online Photoflow – Electrospray Ionisation – Mass Spectrometry

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Light as a non-invasive and clean external stimulus provides a facile route towards macromolecular design. Herein, we demonstrate the scalable synthesis of catalyst-free, visible-light mediated photo-oligomers and -polymers via a step-growth mechanism. Both a batch approach and a continuous photoflow setup are employed to investigate the degree of polymerisation and scalability. Violet blue light at 415 nm triggers [2+2]-cycloadditions of pyrene-chalcone derivative to grow linear step-growth polymers, while subsequent UV-B light irradiation triggers the depolymerisation. The process was monitored online via a photoflow - electrospray ionisation – mass spectrometry setup (ESI-MS). Size Exclusion Chromatography provides additional offline analysis of both the polymerisation and photodegradation over time. By changing the colour of light, photopolymers can be recycled and reshaped, allowing to apply these macromolecular precursors for reversible and photodegradable material design.

Light-driven reactions for macromolecular synthesis receive a growing interest over the last years, because of their inherent cleanliness, non-invasiveness, ease of handling as well as spatiotemporal control.^[1] Photopolymerisations define the class of macromolecular growth mechanisms for which light is employed as an external trigger to promote chain extension.^[2] Most commonly, photoactive initiators, photocatalysts or photosensitizers are used to trigger radical^[3] or ionic^[2, 4] chain-growth polymerisations,^[5] ring-opening metathesis polymerisations^[6] or a combination of those mechanisms,^[7] albeit in a controlled or non-controlled way. Some reports have been published where extension via chain-growth can be established with light without the need of a catalyst or any other external additive.^[8] Recently, not only light generated with lamps, LED's or lasers, but also chemiluminescence is shown to be useful as a photon source to initiate

polymerisation.^[9] Photopolymers that are generated via a step-growth photoligation mechanism are described less, mostly due to their limited control over dispersity and macromolecular size.^[2, 10] Numerous photoligation reactions have been developed and widely employed over the past decades, showing key benefits in polymer synthesis and post-polymerisation modification.^[11] A popular strategy for step-growth polymerisations is to use efficient photo-mediated click reactions, such as thiol-ene coupling^[12] and copper azide-alkyne cycloadditions (CuAAC),^[13] yet they often require additives that need to be removed in an additional purification step. Other studies describe the polyaddition of AB-type photomonomers via light-triggered cycloaddition reactions.^[10b, 14] The couplings are often very selective, result in high yields and require no catalysts or initiators. It is an interesting feature that no additional purification is required to remove any additives that might interfere during consecutive post-polymerisation steps. However, side reactions are often possible – i.e. individual A-A and B-B dimerisations – and subsequently result in uncontrolled chain extensions. Using a single-chromophore system based on AA-type monomers is a more promising concept and eliminates the possibility of cross-reactions. Cinnamates and coumarins are well-known groups to undergo [2+2]-cycloadditions induced by UV-light and have been employed many times to synthesise linear structures and to form cross-linked networks.^[15] Also anthracene derivatives have been introduced into polymer chemistry to design novel architectures triggering [4+4]-photocycloadditions.^[16] More interestingly, cyclodimerisation adducts can also be cleaved by light, typically with a shorter wavelength – i.e. higher energy – regenerating the single chromatic moieties in their uncoupled state.^[17] Cycloreversion is an intriguing concept, as it mediates photodegradability of macromolecular chains. Photoinduced depolymerisations have become more popular over the last years, as growing environmental issues weigh on the use of nondegradable polymers in day-to-day society.^[18] Saito and co-workers described the linear polymerisation of bis-thymine monomers and complete depolymerisation of the corresponding chains by tuning the wavelength range used for irradiation.^[19] Our research group has recently shown that

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

macromolecular size and shape can be controlled with a visible light [2+2]-cycloaddition and cycloreversion reaction by tuning the wavelength of the light source.^[20] This characteristic allows to recycle and react the photoactive moieties several times – promoting the industrial development of green chemistry – and could be featured for recyclable and re-shapable materials.^[21] In addition, visible light provides better penetration compared to shorter wavelengths. More recently, our research group developed an alternative [2+2]-cycloaddition system based on pyrene-chalcones that is reversible and easily scalable in synthesis.^[22] The light-driven system facilitates further applications towards dynamic material design.

For many years, continuous flow reactions have shown advantages in the field of polymer synthesis and design. Due to the high control of the reaction parameters, the setup allows to tune polymer properties and design even better than certain batch analogues.^[23] Continuous flow setups have most certainly proven to be beneficial for light-induced reactions. Indeed, photoreactions in batch processes are mainly limited by the irradiation efficiency.^[24] As described by Beer-Lambert's law, absorption of light and the inherent light gradient induced can be reduced by minimising the irradiation path length. Switching to a narrow tube setup with continuous flow and irradiation overcomes the Beer-Lambert penalty. Not only synthetic methods, but also analysis procedures can be accelerated and automated. Several analysis tools have been coupled to a flow reactor, such as nuclear magnetic resonance, electrospray ionisation - mass spectrometry and size exclusion chromatography, to provide a better understanding of polymerisation kinetics.^[25]

Herein, we describe scalable photopolyaddition polymerisations using the pyrene-chalcone [2+2]-cycloaddition reaction under visible light, without the need of any catalyst or initiator. Subsequently, depolymerisation can be triggered, regenerating the smaller building blocks, which can be re-used for photopolymerisation. By switching from a closed batch to a continuous flow system, online analysis of the photodegradation becomes possible by coupling the photoflow instrument in series to an analytic tool, such as ESI-MS. ESI-MS allows an easy and straightforward read-out of the small oligomeric species present upon irradiation with UV-B light.

Photopolymerisation of bisfunctional pyrene-chalcone blocks

Pyrene-chalcones (PC) can undergo [2+2]-cycloadditions by irradiating with violet blue light ($\lambda_{\text{max}} = 415 \text{ nm}$), in the absence of any photocatalyst or photosensitizer. In addition, they can be readily modified to anchor to a wide variety of functionalities, as well being readily synthesised on a multi-gram scale. Therefore, this photoactive reaction partner is an ideal candidate for the synthesis of photoreversible step-growth polymers. For initial polymerisation studies, a small AA-monomer with end-capped PC was synthesised. bisPC (**Figure 1**) was obtained from 1,10-dibromodecane and a carboxylic acid functional pyrene chalcone with a yield of 91%.

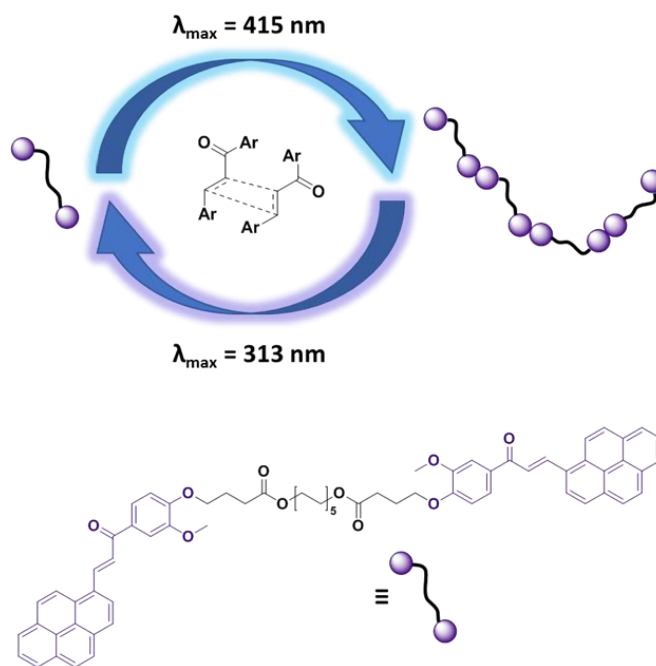


Figure 1: Reversible photopolymerisation using two different wavelengths. An AA-type photomonomer (bisPC) with pendant pyrene-chalcone moieties is used to trigger the polymerisation with violet blue-light at 415 nm. Photodepolymerisation is initiated with UV-B light.

Polymerisations were first monitored in small batch volumes (1 mL) at different concentrations. Degassed mixtures of bisPC of 1, 5, 10 and 100 mg mL⁻¹ in THF were irradiated for several hours to reach the highest degree of polymerisation possible. Size Exclusion Chromatography (SEC) was employed to compare oligomer and polymer formation for the different samples (**Figure 2a**). With an increasing concentration, it was observed that larger oligomers and polymers were formed. The small oligomeric species at higher retention time could be identified via SEC-MS (Figure S1). SEC measurements and subsequent mass spectrometry also revealed the formation of the cyclic monomer after irradiation with visible light, most certainly for the lower concentrated samples. Indeed, characterised by the same exact mass and smaller hydrodynamic volume, intramolecular interactions occur predominantly over intermolecular step-growth polymerisation. At the highest concentration of 100 mg mL⁻¹, bisPC could not be dissolved entirely. However, during the photopolyaddition process, the mixture turned from a turbid suspension into a transparent solution.

Subsequently, the polyaddition reaction was repeated in a photoflow setup, ensuring efficient irradiation of the entire mixture. Again, to achieve the highest degree of polymerisation possible, the mixture was irradiated for several hours. A looped continuous photoflow setup was constructed for this purpose, allowing continuous and long irradiation over time.^[26] With this looped mechanism, there is no need to extend the flow setup and the setup can be kept compact with a single light source. SEC chromatograms were compared to monitor the polymerisation. Even though the flow setup allows more efficient irradiation, there was no significant difference

in the degree of polymerisation for the lower concentration range (10 mg mL^{-1}) when compared to their batch analogue (Figure S2). However, at 100 mg mL^{-1} , barely any significant polyaddition could be observed in the looped flow setup. This could be explained due to the low solubility of the start compound bisPC. Indeed, in flow, the dispersed mixture adhered to the inner surface of the tubing, blocking the incoming photons, preventing further reaction. Additionally, the back pressure of the setup increased over time, decreasing the flow efficiency while gradually blocking the tubing. Even though the setup proved to be limiting for concentrated monomer mixtures, and therefore limiting the degree of polymerisation, a scalable synthesis was possible and more efficient compared to a batch approach. Indeed, with increasing volumes in a batch approach, the light penetration becomes insufficient.

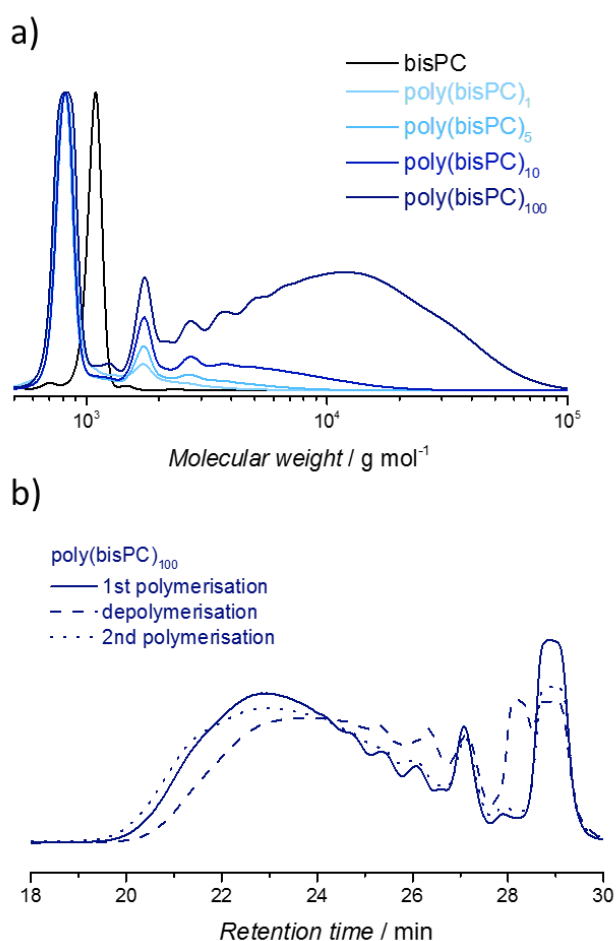


Figure 2: Size exclusion chromatograms of poly(bisPC). **a)** The chromatograms of photopolymerisations of bisPC at different concentrations ($1, 5, 10$ and 100 mg mL^{-1} , $M_n = 1600, 2000, 2600$ and 5300 g mol^{-1} , respectively). An increase in average size can be observed when the monomer concentration increases. **b)** Comparison of the chromatograms after different irradiation states of poly(bisPC)₁₀₀. The larger polymers can degrade under UV-B light, and can be reformed with violet blue light. The number average molecular weight M_n evolves from 5700 to 4700 , back to 5700 g mol^{-1} after the consecutive irradiation steps.

Photoinduced depolymerisation and re-polymerisation

Upon irradiation with UV-B light, the cycloreversion reaction of the pyrene-chalcone adduct can be triggered, inducing photodegradation of oligomers and polymers when built into the backbone. The previously synthesised macromolecules can therefore be reduced in size, making the entire process reversible. Such a polymer is an ideal candidate for the development of photodegradable and recyclable materials, as no additional reagents are required, nor side products are formed. The bisPC was dissolved in THF (degassed) and irradiated with a $3\text{W } 415 \text{ nm}$ LED overnight. Different solution concentrations of 10 and 100 mg mL^{-1} were prepared and irradiated in small volumes (1 mL) to limit inhomogeneous irradiation. Overcoming these issues is mostly relevant for higher concentrations where the light penetration becomes problematic for larger volumes in batch. Subsequently, the polymerised species are irradiated with UV-B light for several hours, allowing to break down the backbone. SEC measurements were performed to follow the size evolution after each irradiation step. Afterwards, the mixtures were re-irradiated with a 415 nm LED overnight and SEC traces were again compared to evaluate the polymerisation behaviour. After UV-B irradiation, it was observed that the oligomers in poly(bisPC)₁₀ degraded back to smaller species. Interestingly, the single repeating unit macrocycles were able to break open again, reforming the single non-cyclic monomer (Figure S3). After re-irradiating with visible light, polymerisation again proceeded, indicating that the entire process is reversible. While chain cleavage was also observed for poly(bisPC)₁₀₀, a significant amount of large polymer chains remained present (Figure 2b). This is due to the limited penetration of the UV-B light at high concentrations of chromophore. Repolymerisation could again be established after irradiation with a $3\text{W } 415 \text{ nm}$ LED. In addition, small solutions of poly(bisPC)₁₀₀ were prepared with 1 mg mL^{-1} of polymer and were irradiated with a UV-B lamp to induce photodegradation. SEC data of irradiation after several time intervals revealed that degradation and the herewith connected average polymer size reduction was increasing over time (Figure S4). Photodegradation thus proved to be more efficient by lowering the polymer concentration of poly(bisPC)₁₀₀. However, there were still residual small oligomers left after long irradiation time. This can be explained as the $[2+2]$ -photoreaction between the pyrene-chalcone moiety and the corresponding adduct is not completely reversible at the chosen concentration range.

Online photodegradation analysis via photoflow-ESI-MS

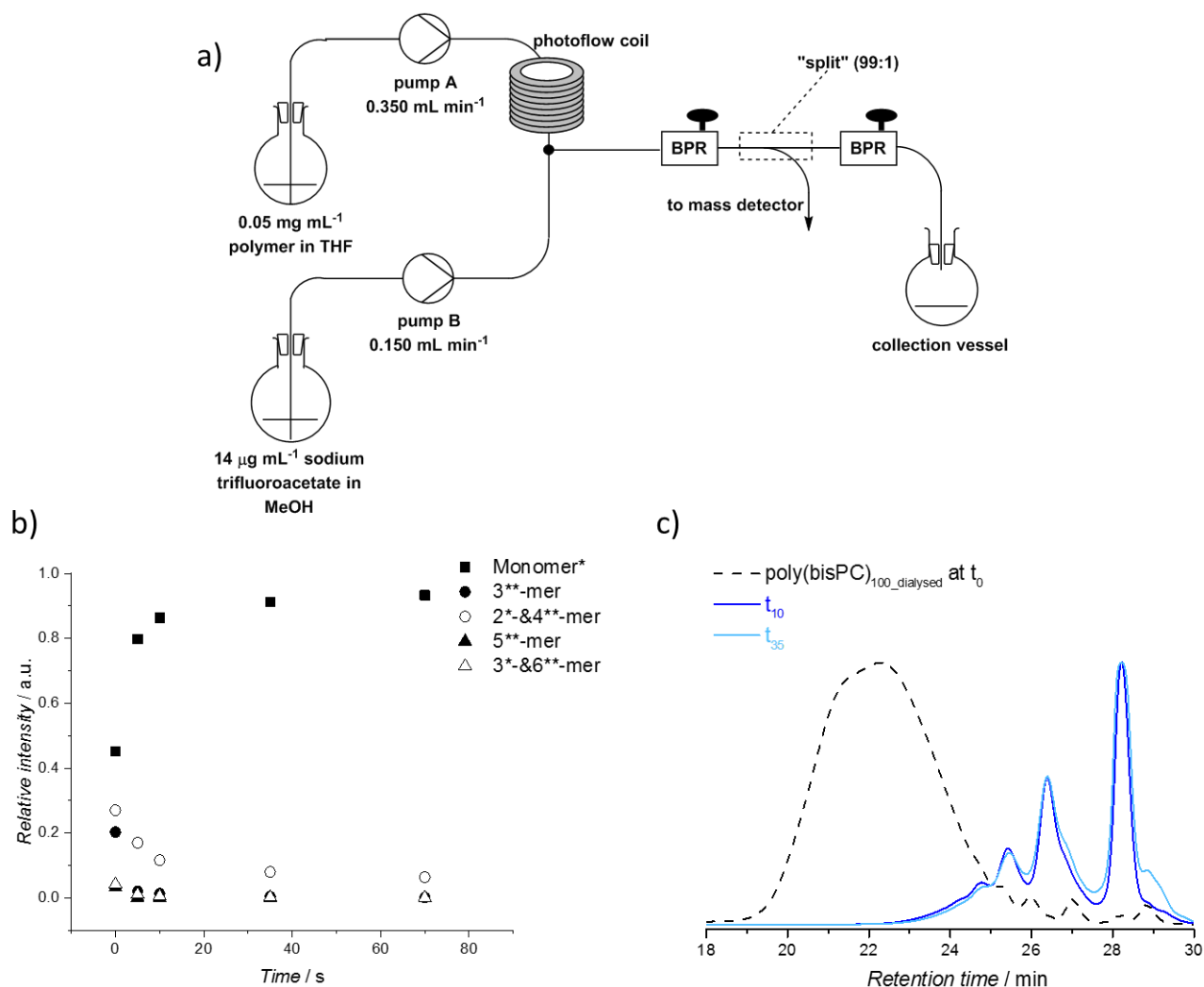


Figure 3: **a)** Schematic overview of the photoflow-ESI-MS setup. A solution of poly(bisPC)₁₀₀ is irradiated with UV-B light for 0, 5, 10, 35 and 70 seconds. Subsequently, the solution is mixed with a dopant stream to promote ionisation in the mass spectrometer. A split with back pressure regulator tunes the stream of material sent into the Orbitrap mass analyser. **b)** Overview of the photodegradation experiments in the flow-MS setup. The relative ion counts of monomer, 2-mer, 3-mer, 4-mer, 5-mer and 6-mer are compared to each other and the fraction of ions ($X_i = \frac{ii}{\sum_{j=1,2,3,4,5,6} I_j}$, where i represent the ion count of species i -mer) are plotted in function of the irradiation time. “*” denotes a single charged sodium adduct, “**” denotes a double charged 2-fold sodium adduct. Cleavage of the oligomeric species can be observed, while more monomeric bisPC appears over longer irradiation. **c)** SEC elugrams of poly(bisPC)₁₀₀ after UV-B irradiation in the flow-MS setup. A comparison is depicted between the initial polymer solution before irradiating (t_0), after 10 seconds (t_{10}) and after 35 seconds (t_{35}) irradiation.

Inducing photoreactions in a continuous photoflow setups facilitates online analysis by coupling the reactor to a suitable analytic tool. Flow-ESI-MS allows an easy and straightforward readout of the species present throughout the reaction. For the first time, we demonstrate the online analysis of photodepolymerisation of linear polymers. A new setup was developed, connecting a Vapourtec E-series photoflow reactor to an Orbitrap Mass Spectrometer (**Figure 3a**). A more detailed description of the instrument settings and flow parameters can be found in the Supporting Information. Poly(bisPC)₁₀₀ was used for the depolymerisation in this model study. To facilitate the readout, the crude material was first dialysed against THF using a 10 kDa MWCO dialysis membrane to enhance the distinction between oligomeric species formed upon irradiation vs. the residual small oligomers present after

polymerisation (refer to the Supporting Information Figure S5). A 0.05 mg mL⁻¹ solution of Poly(bisPC)₁₀₀ was irradiated with UV-B light for various times to map the cycloreversion induced chain cleavage. After irradiation, the product was mixed with methanol, doped with sodium trifluoroacetate to enhance the ionisation for MS. Subsequently, a split was introduced to tune the flow stream to the spectrometer, using a back pressure regulator to alter the outlet. Different irradiation times were achievable by changing the length of the tubing subject to UV-B light while keeping the flow speed constant. A comparison was made between 0, 5, 10, 35 and 70 seconds of irradiation. The summarised results of the photodegradation over different time intervals is depicted **Figure 3b**. Based on the ion count of the species present in each mixture, an increase of the single monomer species was observed, while

simultaneously the relative ion counts of the larger oligomeric species decreased. These trends are in line with what was expected. Indeed, upon triggering the pyrene-chalcone cycloreversion reaction, the monomer is regenerated as shown in the previous section. The longer the irradiation time, the more photocleavage occurs and thus results in a relative increase of the fraction of ions detected in the mass spectrometer. Larger oligomers cleave by UV-B and are not regenerated, and the relative ion count decreases. It should be noted that the obtained data cannot be used for quantifiable degradation analysis. Only a select range of oligomers was analysed, due to the limited measurable m/z range of the instrument. In addition, a bias is introduced related to the ionisation of each oligomeric species. To obtain further insights into the ratio of oligomers present after irradiation, additional SEC measurements were conducted offline (**Figure 3c**). Similarly, it can be observed that the larger oligomeric species were cleaved, and mostly single monomeric units remained present. In addition, a significant fraction of dimer and trimer species could still be distinguished in the SEC elugrams, although these species were mostly suppressed in the MS measurements, due to the ionisation bias. The presence of residual small, oligomeric structures after UV-B irradiation was already observed during the above described depolymerisation experiments. From a statistical perspective, both trends in the SEC and MS measurements can be understood. The larger oligomers have multiple potential cleavage points and will more likely cleave faster, hence the fast decreasing signal of the detector response and the relative ion count. For smaller oligomeric species, less photocleavage points are built into the chain. Therefore, it can be expected that chain scission occurs slower. At the same time, smaller oligomeric species get generated after photocleavage of the larger oligomeric species. Hence, a less drastic change in relative ion abundance is likely, as seen in **Figure 3b**. As the single monomer repeating unit can only be generated after UV-B irradiation and cannot cleave any further, a large increase in both the relative ion count and SEC detector response is observed.

Conclusions

We successfully demonstrated the synthesis of linear step-growth polymers via photoligation with visible light. [2+2]-cycloaddition reactions can be employed to gradually increase the chain length, with increasing degree of polymerisation achievable at higher monomer concentrations. Critically, scalable synthesis becomes possible by switching from a conventional batch approach to a photoflow setup. Not only polymerisation, but also photodepolymerisation is possible under light. Smaller building blocks can be re-obtained and recycled for subsequent polymerisations. The reversible pyrene-chalcone dimerisation is applicable on a multigram scale and is therefore a suitable candidate for recyclable material design. Photoflow further assists in the photodegradation analysis via online mass spectrometry.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

C.B.-K. acknowledges a Laureate Fellowship from the Australian Research Council (ARC) enabling his photochemical research program. Key additional support from the Queensland University of Technology (QUT) is gratefully acknowledged. The authors further acknowledge the Central Analytical Research Facility (CARF) at QUT, which is generously supported by the Faculty of Science and Engineering.

Notes and references

- [1] K. Jung, N. Corrigan, M. Ciftci, J. Xu, S. E. Seo, C. J. Hawker, C. Boyer, *Advanced Materials* **2020**, *32*, 1903850.
- [2] H. Lai, J. Zhang, F. Xing, P. Xiao, *Chemical Society Reviews* **2020**, *49*, 1867-1886.
- [3] a) X. Pan, M. A. Tasdelen, J. Laun, T. Junkers, Y. Yagci, K. Matyjaszewski, *Progress in Polymer Science* **2016**, *62*, 73-125; b) S. Dadashi-Silab, S. Doran, Y. Yagci, *Chemical Reviews* **2016**, *116*, 10212-10275; c) M. Chen, M. Zhong, J. A. Johnson, *Chemical Reviews* **2016**, *116*, 10167-10211.
- [4] a) S. Shi, C. Croutxé-Barghorn, X. Allonas, *Progress in Polymer Science* **2017**, *65*, 1-41; b) Q. Michaudel, V. Kottisch, B. P. Fors, *Angewandte Chemie International Edition* **2017**, *56*, 9670-9679.
- [5] N. Corrigan, J. Yeow, P. Judzewitsch, J. Xu, C. Boyer, *Angewandte Chemie International Edition* **2019**, *58*, 5170-5189.
- [6] O. Eivgi, N. G. Lemcoff, *Synthesis* **2018**, *50*, 49-63.
- [7] a) T. Krappitz, K. Jovic, F. Feist, H. Frisch, V. P. Rigoglioso, J. P. Blinco, A. J. Boydston, C. Barner-Kowollik, *Journal of the American Chemical Society* **2019**, *141*, 16605-16609; b) J. Shao, Y. Huang, Q. Fan, *Polymer Chemistry* **2014**, *5*, 4195-4210.
- [8] a) T. G. McKenzie, Q. Fu, E. H. H. Wong, D. E. Dunstan, G. G. Qiao, *Macromolecules* **2015**, *48*, 3864-3872; b) J. Yeow, O. R. Sugita, C. Boyer, *ACS Macro Letters* **2016**, *5*, 558-564; c) S. Shanmugam, J. Cuthbert, T. Kowalewski, C. Boyer, K. Matyjaszewski, *Macromolecules* **2018**, *51*, 7776-7784.
- [9] a) C. Wang, X. Meng, Z. Li, M. Li, M. Jin, R. Liu, Y. Yagci, *ACS Macro Letters* **2020**, *9*, 471-475; b) J. Zhu, Y. Zhu, Z. Li, Z. Yu, X. Guan, R. Liu, Y. Yagci, *Macromolecular Rapid Communications* **2020**, *41*, 2000004; c) N. De Alwis Watuthantrige, M. L. Allegranza, M. T. Dolan, A. J. Kloster, M. Kovaliov, S. Averick, D. Konkolewicz, *Angewandte Chemie International Edition* **2019**, *58*, 11826-11829; d) K. B. Kockler, H. Frisch, C. Barner-Kowollik, *Macromolecular Rapid Communications* **2018**, *39*, 1800516.
- [10] a) G. Yilmaz, Y. Yagci, *Progress in Polymer Science* **2020**, *100*, 101178; b) S. Hurrell, A. S. Goldmann, H. Gliemann, H. Mutlu, C. Barner-Kowollik, *ACS Macro Letters* **2018**, *7*, 201-207.
- [11] B. T. Tuten, S. Wiedbrauk, C. Barner-Kowollik, *Progress in Polymer Science* **2020**, *100*, 101183.
- [12] a) C. E. Hoyle, A. B. Lowe, C. N. Bowman, *Chemical Society Reviews* **2010**, *39*, 1355-1387; b) A. E. Rydholm, C. N. Bowman, K. S. Anseth, *Biomaterials* **2005**, *26*, 4495-4506.
- [13] B. J. Adzima, Y. Tao, C. J. Kloxin, C. A. DeForest, K. S. Anseth, C. N. Bowman, *Nature Chemistry* **2011**, *3*, 256-259.
- [14] D. Estupiñán, T. Gegenhuber, J. P. Blinco, C. Barner-Kowollik, L. Barner, *ACS Macro Letters* **2017**, *6*, 229-234.

- [15] a) P. Gupta, S. R. Trenor, T. E. Long, G. L. Wilkes, *Macromolecules* **2004**, *37*, 9211-9218; b) S. R. Trenor, A. R. Shultz, B. J. Love, T. E. Long, *Chemical Reviews* **2004**, *104*, 3059-3078.
- [16] a) J.-F. Xu, Y.-Z. Chen, L.-Z. Wu, C.-H. Tung, Q.-Z. Yang, *Organic Letters* **2013**, *15*, 6148-6151; b) J. Van Damme, O. van den Berg, J. Brancart, L. Vlamincq, C. Huyck, G. Van Assche, B. Van Mele, F. Du Prez, *Macromolecules* **2017**, *50*, 1930-1938.
- [17] G. Kaur, P. Johnston, K. Saito, *Polymer Chemistry* **2014**, *5*, 2171-2186.
- [18] T. Chen, H. Wang, Y. Chu, C. Boyer, J. Liu, J. Xu, *ChemPhotoChem* **2019**, *3*, 1059-1076.
- [19] P. Johnston, C. Braybrook, K. Saito, *Chemical Science* **2012**, *3*, 2301-2306.
- [20] H. Frisch, K. Mundsinger, B. L. J. Poad, S. J. Blanksby, C. Barner-Kowollik, *Chemical Science* **2020**, *11*, 2834-2842.
- [21] Q. Chen, Q. Yang, P. Gao, B. Chi, J. Nie, Y. He, *Industrial & Engineering Chemistry Research* **2019**, *58*, 2970-2975.
- [22] M. Van De Walle, K. De Bruycker, J. P. Blinco, C. Barner-Kowollik, *Angewandte Chemie International Edition* **2020**, <https://doi.org/10.1002/anie.202003130>.
- [23] a) J. Gardiner, C. H. Hornung, J. Tsanaktsidis, D. Guthrie, *European Polymer Journal* **2016**, *80*, 200-207; b) E. Mastan, J. He, *Macromolecules* **2017**, *50*, 9173-9187; c) C. H. Hornung, C. Guerrero-Sanchez, M. Brasholz, S. Saubern, J. Chiefari, G. Moad, E. Rizzardo, S. H. Thang, *Organic Process Research & Development* **2011**, *15*, 593-601; d) A. Kuroki, I. Martinez-Botella, C. H. Hornung, L. Martin, E. G. L. Williams, K. E. S. Locock, M. Hartlieb, S. Perrier, *Polymer Chemistry* **2017**, *8*, 3249-3254; e) M. H. Reis, F. A. Leibfarth, L. M. Pitet, *ACS Macro Letters* **2020**, *9*, 123-133; f) N. Zaquen, J. Yeow, T. Junkers, C. Boyer, P. B. Zetterlund, *Macromolecules* **2018**, *51*, 5165-5172; g) M. Van De Walle, K. De Bruycker, T. Junkers, J. P. Blinco, C. Barner-Kowollik, *ChemPhotoChem* **2019**, *3*, 225-228; h) B. Wenn, T. Junkers, *Macromolecules* **2016**, *49*, 6888-6895.
- [24] a) Y. Su, N. J. W. Straathof, V. Hessel, T. Noël, *Chemistry – A European Journal* **2014**, *20*, 10562-10589; b) D. Cambié, C. Bottecchia, N. J. W. Straathof, V. Hessel, T. Noël, *Chemical Reviews* **2016**, *116*, 10276-10341.
- [25] a) J. J. Haven, T. Junkers, *European Journal of Organic Chemistry* **2017**, *2017*, 6474-6482; b) J. J. Haven, J. Vandenbergh, T. Junkers, *Chemical Communications* **2015**, *51*, 4611-4614.
- [26] E. Baeten, M. Rubens, K. N. R. Wuest, C. Barner-Kowollik, T. Junkers, *Reaction Chemistry & Engineering* **2017**, *2*, 826-829.