Photocatalysis **Hot Paper**

Temporal Regulation of PET-RAFT Controlled Radical Depolymerization

Valentina Bellotti, Hyun Suk Wang, Nghia P. Truong, Roberto Simonutti, and Athina Anastasaki*

Abstract: A photocatalytic RAFT-controlled radical depolymerization method is introduced for precisely conferring temporal control under visible light irradiation. By regulating the deactivation of the depropagating chains and suppressing thermal initiation, an excellent temporal control was enabled, exemplified by several consecutive "on" and "off" cycles. Minimal, if any, depolymerization could be observed during the dark periods while the polymer chain-ends could be efficiently re-activated and continue to depropagate upon re-exposure to light. Notably, favoring deactivation resulted in the gradual unzipping of polymer chains and a stepwise decrease in molecular weight over time. This synthetic approach constitutes a simple methodology to modulate temporal control during the chemical recycling of RAFT-synthesized polymers while offering invaluable mechanistic insights.

Reversible deactivation radical polymerization (RDRP), also referred to as controlled radical polymerization (CRP), has enabled the preparation of previously inaccessible materials by allowing precise control over the molecular weight, dispersity, architecture, sequence and end-group fidelity.[1–6] The current state-of-the-art methodologies confer control over the polymerization by manipulating the activation/deactivation equilibrium between active and dormant species. This control can be achieved either through reversible termination as in the case of atom transfer radical polymerization (ATRP) or via degenerative transfer like in reversible addition-fragmentation chain-transfer (RAFT) polymerization.[7–9] However, current synthetic challenges

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require not only controlled polymerizations and functional materials but also on-demand access to certain properties and performance. To realize this, various external stimuli, such as light,[10–12] mechanical force,[13,14] and applied voltage,[15,16] have been employed to reversibly turn the polymerization "on" and "off". Light in particular combines most of the characteristics of an ideal system for temporal and spatial control; it is a widely available, non-invasive and low-cost component that can reversibly switch processes by simply switching the light "on" or "off". Moreover, light-induced polymerizations exhibit faster polymerization rates compared to their thermal counterparts, produce polymers with enhanced end-group fidelity and narrower molar mass distributions and enable precise control over reaction kinetics by modulating the intensity of irradiation.[17–22] Despite the immense advantages and possibilities imparted by light, it has been primarily exploited for controlled radical polymerizations[23] and little attention has been directed to light-driven depolymerizations.[24] To date, the vast majority of current depolymerization approaches rely solely on heat as an external stimulus.[25–34] For instance, Matyjaszewski and co-workers have developed a series of elegant iron and copper-based chemical recycling strategies that allow for the rapid depolymerization of both bulky and not-bulky ATRP-synthesized polymers at 170 °C.[25,27,35] In the RAFT arena, Gramlich's group first demonstrated the possibility of RAFT-synthesized brush polymers to undergo depolymerization at polymerization-relevant temperatures (i.e. 70 °C).[31] Inspired by this work, our group then exploited thermodynamically favorable conditions (i.e. 120 °C and high dilution) to expand the depolymerization scope to non-bulky polymers such as poly(methyl methacrylate) while achieving high depolymerization yields.[26,28] Sumerlin's group and our group independently showed that either UV or visible irradiation can be employed, in conjunction with heat, to enhance the rate of radical generation and accelerate depolymerization.[36,37] However, upon switching the light "off", the depolymerization would continue to depropagate in the dark due to the prominent contribution of the thermal depolymerization, thereby prohibiting the possibility for temporal control. In addition, the vast majority of present chemical recycling approaches report a negligible, if any, M_n shift as the depolymerization proceeds.[26,28,36–39] This suggests a rather uncontrolled depolymerization whereby upon chain-end activation, the polymer chain undergoes a rapid and complete unzipping back to monomer in the absence of significant deactivation events. This uncontrolled nature can be directly compared

to conventional radical polymerization whereby upon radical generation, and in the absence of deactivation, the chains instantly reach their final molecular weight. We reasoned that the lack of sufficient deactivation during the chemical recycling of polymers synthesized by RDRP further restricts the possibility for spatial and temporal control.

Herein, we introduce a photocatalytic RAFT-controlled radical depolymerization whereby chain activation is only possible when the light is switched "on" while thermal initiation during the "off" periods is completely eliminated.

Key to this strategy is to ensure sufficient deactivation throughout the depolymerization in order to preserve high end-group fidelity (i.e. polymer chains are continuously capped by the CTA). The concept is illustrated in Figure 1.

Poly(methyl methacrylate) (PMMA) was synthesized via a thermal RAFT polymerization protocol (Figures S2–3) and was chosen as the model polymer for our depolymerization studies. First, we sought to investigate the possibility of temporal control in a traditional depolymerization system that operates at a high dilution (1 mM repeat unit
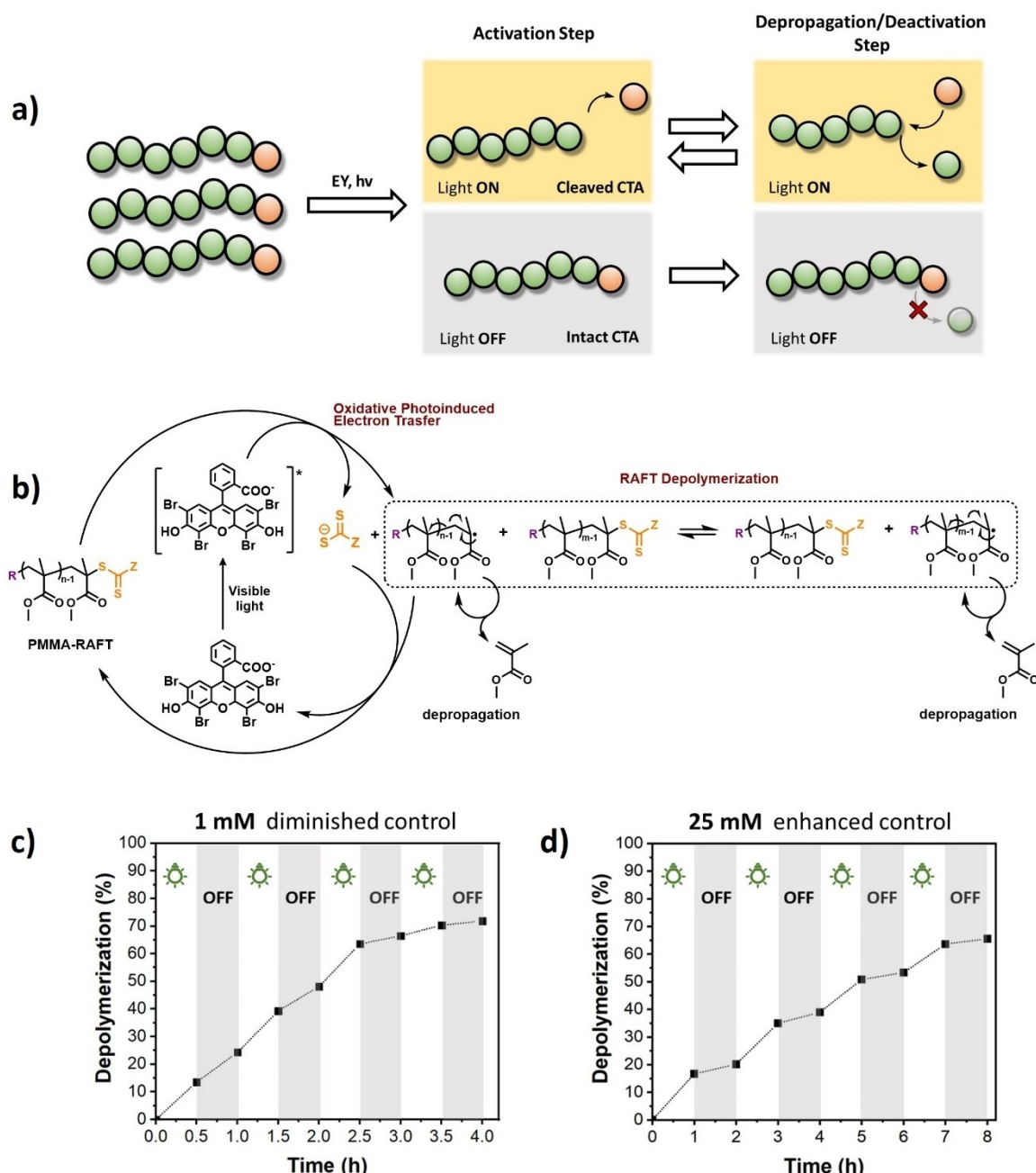

Figure 1. a) Representation of temporal controlled PET-RAFT depolymerization demonstrating continuous deactivation of the polymer chains. b) Reaction Scheme of PET-RAFT controlled depolymerization catalyzed by Eosin Y. b) Graphical scheme of temporal controlled PET-RAFT depolymerization demonstrating continuous deactivation of the polymer chains. On the bottom, "on"–"off" experiments of photo-catalyzed depolymerization at 100 °C with c) 1 mM and d) 25 mM initial repeat unit (RU) concentrations are illustrated.

concentration).[26] In the presence of a catalytic amount of Eosin Y (100 ppm) and under green light irradiation, we conducted a photothermal depolymerization at 100 °C in a homemade *ad hoc* photo-thermal reactor. The light wavelength was carefully selected by kinetic studies given that some catalysts exhibit efficient performance at wavelengths that do not match their maximum absorption (Figure S1).[40] Several intermittent light "on" and "off" cycles were performed. The reaction was first exposed to green light for 30 minutes resulting in approximately 14 % of depolymerization conversion. However, upon removal of the light source, the depolymerization continued at a comparable rate reaching a total of 25 % of conversion in the next 30 minutes. In a similar vein, negligible, if any, changes in the rate of depolymerization were observed during the subsequent "on" and "off" cycles (Figure 1c). This data suggests that minimal, if any, temporal control could be obtained. To understand this further, we performed a control experiment where the depolymerization was conducted under exclusively thermal conditions yielding 84 % of regenerated monomer, as detected by ^{1}H nuclear magnetic resonance (NMR), within 6 h. Considering that the light-induced depolymerization also resulted in a comparable conversion (i.e. 86 %) within a similar timeframe, we concluded that thermal initiation is the main pathway for end-group removal under the conditions studied. A detailed kinetic study under light irradiation was also conducted revealing a very small M_n shift towards lower molecular weights throughout the depolymerization (Figure 2a–c). In particular, at 86 % of final depolymerization conversion, an M_n shift of only 12 % was observed. This result is in line with the vast majority of depolymerization reports of RDRP-synthesized

polymers and can be attributed to insufficient deactivation.[24] We thus speculated that under the employed conditions, depropagation is significantly favored over deactivation leading to an uncontrolled depolymerization whereby the polymer chains fully unzip back to monomer. We hypothesized that by enhancing the deactivation of the polymer chain-ends during the depolymerization, a more controlled pathway could be triggered where the monomers would unzip one by one, thus resembling the true reversal of a RDRP. At the same time, a more efficient deactivation would allow for end-group preservation (i.e. through constant capping of the radical chain-ends) during the dark periods and thus potentially enable an improved temporal control.

To examine this hypothesis, we repeated the temporal control experiment with a 25-fold increased concentration under otherwise identical conditions (Figure 1d). A slower depolymerization profile was observed, albeit with a significantly improved temporal control. Specifically, by exposing the reaction mixture to light irradiation for 1 h, 18 % of conversion was achieved. After removal of the light source for another 1 h, only 2 % of conversion could be detected thus suggesting that thermal initiation was significantly suppressed probably due to enhanced deactivation. The same trend continued for the remaining cycles and up to a total of approximately 70 % of depolymerization conversion. To confirm whether the observed enhancement in temporal control is the result of a more efficient deactivation, light-induced depolymerization kinetics at 25 mM were performed (Figure 2d–f). A distinct depolymerization profile was immediately observed with the molecular weight clearly shifting towards lower molecular weight as the depolymeri-
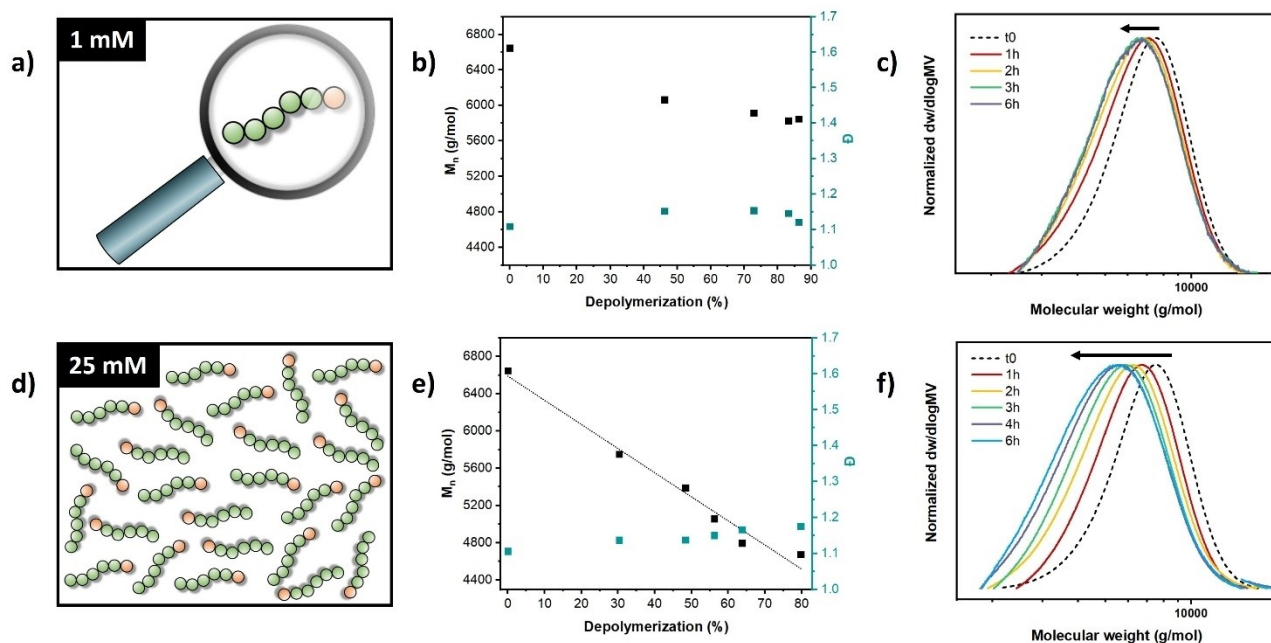

Figure 2. The photo-catalyzed depolymerization of PMMA-DTB at 100 °C with initial monomer RU concentrations of a) 1 mM. and d) 25 mM. B) and e) show the evolution of molecular weight and dispersity with depolymerization conversion and c) and f) illustrate the evolution of the molecular weight distributions, respectively.

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zation progressed. M_n reduced by up to 41% at high depolymerization conversions (i.e. 80%) while the molar mass dispersity remained fairly narrow. These findings indicate a uniform unzipping of the polymer chain-ends which was attributed to the enhanced deactivation achieved at higher macroCTA concentrations. Nonetheless, the control depolymerization experiment under heat still revealed ≈48% of thermal contribution within 24 h. Taken altogether, our results suggest that deactivation is a key criterion in suppressing thermal initiation. However, further optimization is required in order to identify conditions that would confer a perfect temporal control.

We thus decided to further examine the effect of the macroCTA concentration. In principle, an even faster deactivation rate would result in a higher M_n shift and ultimately an improved temporal control. Indeed, when the depolymerizations were conducted at either 50 mM or 100 mM concentration, the M_n shift more closely matched the theoretical values, as can be shown in Figure S4. As such, it was concluded that more efficient deactivation takes place at higher concentrations, in line with our earlier hypothesis. However, it is worth noting that higher concentrations lead to slower depolymerization kinetics due to increased competition reactions such as deactivation. For instance, at 100 mM, an 18% of depolymerization conversion is accompanied by the theoretically expected 18% M_n shift, which is a sign of a truly controlled depolymerization. Unfortunately, the significant deceleration in the depolymerization rate led to only 18% of conversion within 4 h (37% of conversion was noticed in 24 h). Encouragingly, depolymerization exclusively triggered by heat within 24 h was only found to be 15% thus suggesting once more that deactivation and thermal initiation are interconnected. It is highlighted that in an ideal scenario, a perfect temporal control would be desirable but without severely compromising the overall depolymerization conversion. As such, finding a balance between efficient deactivation, suppressed thermal depolymerization, and appreciable depolymerization rate is of paramount importance. For example, at 25 mM a significantly improved temporal control was observed without sacrificing the overall depolymerization conversion (80% within 6 h as opposed to 86% achieved for the 1 mM comparison). At 50 mM, a system with more pronounced deactivation, the temporal control improved further with only 1.5% of conversion observed during 1 h in the dark (Figure S5). At the same time, an appreciable depolymerization conversion of approximately 57% was maintained within 8 h. However, considering that both the 50 mM and 100 mM control experiments revealed a significant thermal contribution of 30 and 15% respectively within 24 h, it was concluded that deactivation alone may not be able to fully eliminate thermal initiation and as such an alternative strategy was explored.

Next, our attention was directed to the depolymerization temperature as it plays a key role from a thermodynamic perspective ($\Delta G = \Delta H - T\Delta S$). Although decreasing the temperature should not significantly affect the deactivation of the polymer chain ends, it will though certainly impact the depolymerization conversion. However, a lower depolymeri-

zation temperature may also suppress the thermal initiation and as such trigger a truly photo-induced catalytic depolymerization and enable a perfect temporal regulation. Considering the advantages of photocatalysis, to activate the RAFT chain-end at lower temperatures, we examined the depolymerization kinetics at various temperatures. Here it is worth recalling that the photothermal depolymerization at 100°C and 1 mM reached up to 86% of conversion. Instead, the thermal contribution during the same time frame was 48% thus explaining the lack of a perfect temporal control. By decreasing the temperature to 90°C, a somewhat slower kinetic profile was recorded and a final conversion of 60% was obtained (Figure S6). Notably, the thermal initiation could be almost eliminated with only 1.7% of conversion attained in 24 h. Although further lowering the depolymerization temperatures to 80 and 70°C led to the complete elimination of the thermal contribution (i.e. 0% in 24 h for both cases), it also dramatically decelerated the depolymerization rate with the final depolymerization conversions reaching 37% and 19% respectively. Nevertheless, the experiments at 90, 80 and 70°C constitute the first examples of a true photocatalytic-triggered depolymerization. Key to this success is the use of a photocatalyst which allows for the chain-end activation even at lower temperatures. Considering that the photothermal reactions at 90°C showed negligible, if any, thermally-initiated depolymerization while maintaining an appreciable depolymerization rate, we envisioned that it would be an ideal candidate for the temporal control experiments. To investigate this, five consecutive "on"–"off" cycles were subsequently performed using intermittent light and dark exposure for alternating one hour periods. Zero depolymerization conversion was achieved in all the dark periods, thus confirming a truly perfect temporal control (Figure 3). In addition, SEC traces showed a gradual shift to lower molecular weights when the light was "on" while no M_n shift could be witnessed in the dark, thus further validating the complete cessation of the depolymerization when the light was "off". Excellent temporal control could also be attained when longer dark periods were tested (2 h and 4 h each, Figure S7), further confirming the versatility of the system. Last but not least, an equally efficient temporal control accompanied by a gradual decrease in the M_n was observed in both dioxane and DMSO (Figure 3c), different polymethacrylates (i.e. poly(benzyl methacrylate) and poly(butyl methacrylate)), and PMMA with a trithiocarbonate end-group (Figure S8–9), thus further expanding the scope of our approach.

To summarize, we have developed a photocatalytic RAFT controlled depolymerization that confers perfect temporal control while also enabling the gradual unzipping of the polymer chains. Key to our strategy was to establish conditions which favor deactivation over depropagation and suppress thermal initiation while maintaining an appreciable depolymerization rate. We anticipate that in analogy to the myriad opportunities enables by controlled photo-mediated polymerizations, the developed photo catalytic controlled depolymerization methodology offers a plethora of additional opportunities.
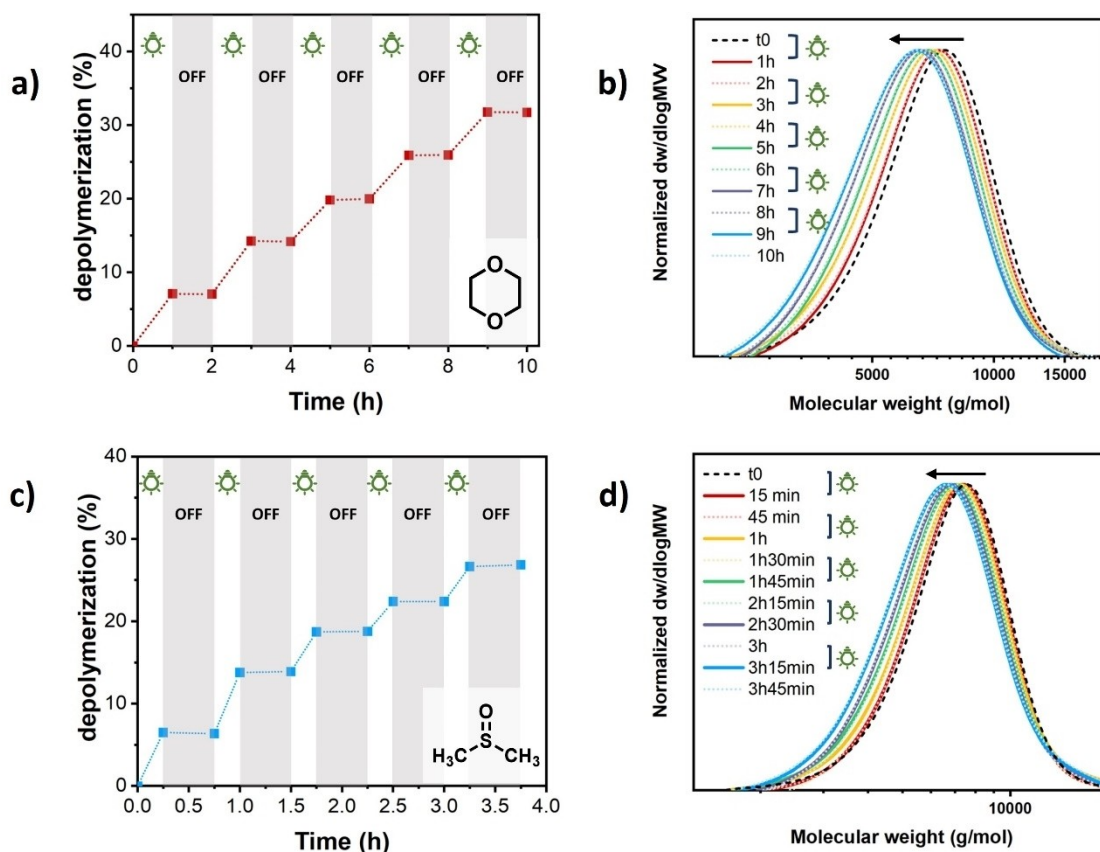
Figure 3. Temporal control experiments for photo-catalyzed depolymerization at 90 °C using a $[RU]_0$ of 25 mM. Kinetic plots show the evolution of the depolymerization during on and off periods (a, c) and SEC plots show the evolution of the molecular weight distribution (b, d) for reactions performed in dioxane and DMSO, respectively.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Depolymerization · PET-RAFT · Photocatalysis · Reverse RDRP · Temporal Control

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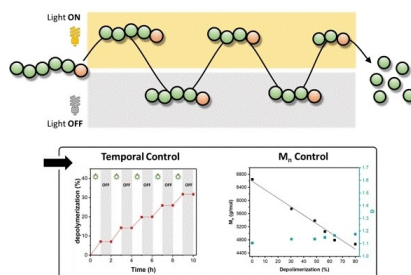
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Photocatalysis

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Temporal Regulation of PET-RAFT Controlled Radical Depolymerization

Precise temporal control under visible irradiation has been achieved through a photocatalytic RAFT chemical recycling methodology. Depolymerization could be easily initiated by switching "on" the light, whereas negligible monomer regeneration was observed in the dark. This outstanding characteristic was possible by fine regulation of the deactivation of the depropagating chain and by finally suppressing thermal initiation of the chains.