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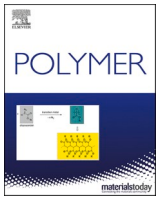

Visible light-induced photo-radical ring-opening copolymerization of thionolactone and acrylates

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A B S T R A C T

Radical ring-opening (co)polymerization (RROP) provides an accessible method for synthesizing main chain degradable vinyl polymers. Although the applications of reversible deactivation radical polymerization (RDRP) into RROP have been reported, the use of photo-mediated RDRP methods has received less attention than the thermal process. Here, photo-RROP of the thionolactone dibenzo [c,e]-oxepine-5(7H)-thione (DOT) and methyl acrylate (MA) was studied using photo-iniferter (PI) reversible addition-fragmentation (chain) transfer (RAFT) polymerization at ambient temperature without external radical initiators or photocatalysts. Despite the occurrence of some side reactions including desulfurization-oxygenation and O–S isomerization of DOT promoted by photoexcited thiocarbonyl groups, polymers with thioester linkages in the backbone were prepared, which degraded in the presence of amines and bleach.

1. Introduction

Degradable vinyl polymers are of increasing interest for many applications ranging from drug delivery, medical devices, sustainable materials, and anti-biofouling coating [1–4]. While the degradation of pendant groups in vinyl polymers generates a small loss of polymers molecular weight, the degradation of the main chain/backbone disintegrates polymers into small size fragments [5–8]. The synthesis of backbone degradable vinyl polymers can be achieved through three general strategies: 1) polymerization from degradable initiators/chain transfer agents [9–12], 2) radical ring-opening (co)polymerization (RROP) of cyclic monomers such as cyclic ketene acetals, allylic sulfides/sulfones, lipoic acid, and thionolactone [13–20], 3) copolymerization with reactive monomers that generates midchain radicals and induces β-carbon fragmentation [21–23]. In addition, depolymerization of vinyl polymers can be achieved above ceiling temperature (T_c) or below equilibrium monomer concentration (M_{eq}) at higher temperatures (>100 °C) [24–26].

Introduced separately by Roth and Gutekunst [27,28], thionolactone dibenzo [c,e]-oxepine-5(7H)-thione (DOT) has seen increasing interest as a versatile monomer for RROP to form degradable vinyl polymers via formation of thioester linkages in the backbone. The versatility of DOT in terms of relatively easy synthesis, diverse copolymerizability, and facile degradation under benign conditions (*i.e.*, aminolysis, thiolysis, methanolysis and oxidation) has inspired its use in various applications spanning from drug delivery [29], pressure sensitive adhesive [30], degradable networks [31], and 3D printing resin additive [32]. DOT was polymerized using free radical polymerization (FRP) [27,33], thermally initiated reversible addition fragmentation (RAFT) polymerization [28,34], nitroxide mediated polymerization (NMP) [29,35], and atom transfer radical polymerization (ATRP) [36]. It was copolymerized with acrylates [27,28], acrylamides [27], acrylonitrile [27], styrene [33], isoprene [29], maleimides [37], and methacrylates [38]. Other thionolactone derivatives were also copolymerized with vinyl esters [39,40] and styrene [41,42]. All the above methods require high temperature (>60 °C) for the polymerization, and most require external radical initiators which lead to unfunctionalized polymer chains.

The photo-mediated controlled radical polymerization (CRP)/reversible deactivation radical polymerization (RDRP) has witnessed remarkable progress leading to the development of methods such as photo-ATRP [43–45], photo-induced electron/energy transfer (PET)--RAFT [46], photo-iniferter (PI)-RAFT [47], and photo mediated iodine polymerization [48,49]. The benefits of light such as spatial and temporal control, energy efficiency, short reaction time, and oxygen tolerance have facilitated the formation of well-defined polymers by photo-RDRP [50–55]. However, RROP of thionolactone via photo-RDRP has not been yet investigated and the only examples of applications of photo-RDRP in RROP (photo-RDRP-RROP) for generating degradable vinyl polymers are limited to cyclic ketene acetals and allylic sulfide/sulfone macrocycles [56–58], albeit examples of

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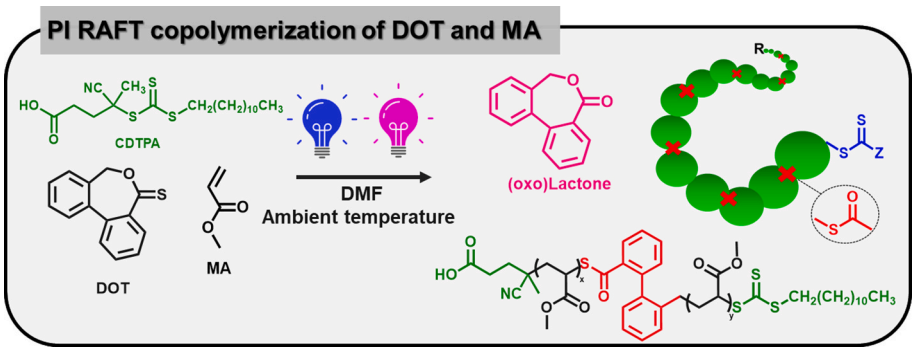

Fig. 1. Radical ring-opening polymerization (RROP) of DOT with PI RAFT polymerization for the preparation of backbone degradable vinyl polymers.

photo-RDRP-RROP of other cyclic monomers (*i.e.*, vinylcyclopropanes, 4-methylene-1,3-dioxolane, or cyclic allylic sulfides) which generate non-degradable backbones were described [59–62].

In this study, we report PI RAFT copolymerization of methyl acrylate (MA) and DOT with 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl] pentanoic acid (CDTPA) as a chain transfer agent (Fig. 1). We were especially interested in using PI RAFT due to its merits including ambient temperature polymerization, photo-catalyst-free, visible light photo-activation, absence of exogenous radical initiators, and moderate oxygen tolerance [47,63]. It was expected that metal- and photocatalyst-free conditions of PI RAFT would minimize the side reactions that are common for photoreactions of thiocarbonyl groups [64]. The side reactions of DOT in the photoexcited conditions were comprehensively investigated to pave the way for future extension of photo-mediated RDRP methods to other thionolactone derivatives.

2. Results and discussion

Photophysical properties of DOT and CDTPA. Considering our aim to use RAFT polymerization for the copolymerization of DOT and MA, which also relies on thiocarbonyl chemistry, it was necessary to initially evaluate and compare the photophysical properties of DOT and CDTPA. When the UV-VIS spectra of DOT were compared to CDTPA, it was noticed that both DOT and CDTPA absorb in a similar region in the UV (λ_{max} = 280 nm and 299 nm for DOT and CDTPA, respectively) and blue region (λ_{max} = 433 nm and 450 nm for DOT and CDTPA, respectively), which correspond to their π→π* and n→π* transitions (Fig. 2A&B). However, the molar extension coefficient of n→π* transition of DOT was significantly higher than CDTPA (ε = 453.2 $M^{-1}Cm^{-1}$ and 30.7 $M^{-1}Cm^{-1}$ at λ_{max} for DOT and CDTPA, respectively), giving rise to the characteristic dark yellow color of DOT versus the light-yellow color of CDTPA (Fig. 2C). Notably, the molar extension coefficient of DOT and CDTPA are similar at the UV region ($\varepsilon = 1.17 \times 10^4$ $M^{-1}Cm^{-1}$, 1.04×10^4 at λ_{max} for DOT and CDTPA, respectively) suggesting that both DOT and CDTPA could absorb equivalent photons at UV region to undergo photochemical reactions.

PI RAFT copolymerization of DOT and MA with blue light. Because PI RAFT polymerization employing CDTPA is best operative under blue light irradiation [65], we performed the first experiments with a commercial Kessil blue light source (456 nm, 75 mW/cm^2). DOT

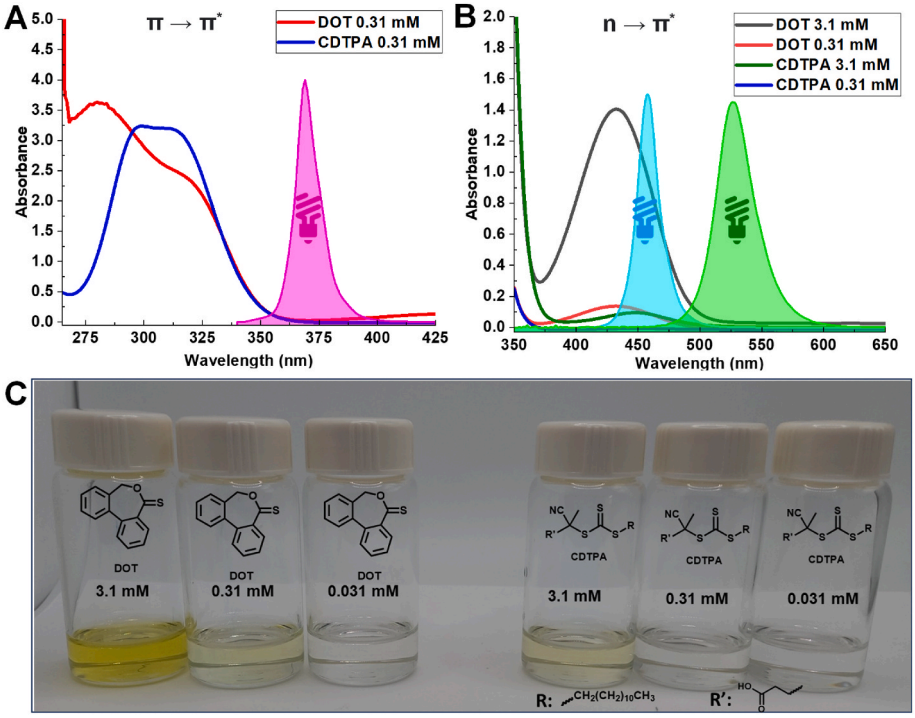

Fig. 2. UV-VIS spectra of π→π* (A) and n→π* (B) transition of DOT and CDTPA compared to the emission of UV (370 nm), blue (456 nm) and green (525 nm) light source and digital image (C) of DOT and CDTPA in DMF. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 1
Properties of copolymers synthesized by RROP-PI RAFT copolymerization of DOT and MA.[a].

Entry	M/DOT	Light (nm)	Time (hr)	[b]Conv (%) (M/DOT)	[c]$M_{n,the}$ (x1000)	[d]$M_{n,app}$ (x1000)	[d]$Đ$
1	100/2.5	456	24	88/>95	8.5	4.5	1.28
2	100/5	456	27	76/>95	8.0	5.1	1.25
3	100/0	456	17	95>/-	8.2	10.9	1.08
4[e]	100/2.5	456	24	0/>95	–	–	–
5	100/10	456	43	68/>95	8.5	0.47	1.98
6[f]	100/2.5	456	27	83/>95	42.4	15.6	1.44
7	100/5	370	45	93/>95	9.5	4.4	1.67
8	100/0	525	7	0/30	–	–	–
9[g]	100/2.5	525	48	58 > 95	–	–	–

(a) PI RAFT polymerization was carried out using CDTPA as a chain transfer agent in DMF using Kessil lights: Blue (456 nm, 75 mW/Cm^2), UV (370 nm, 100 mW/Cm^2) and green (525 nm, 75 mW/Cm^2). Temperature of the reactor during the polymerization was 37 °C. $[CDTPA]_0 = 58$ mM, $[MA]_0 = 5.8$ M. (b) Monomer conversion was determined by using ^{1}H NMR spectroscopy. DOT conversion was based on the reduction of ^{1}H NMR peaks at 5.15 and 5.45 p.m. and represent the conversion to both thioester in the polymer and conversion to other side products. (c) Calculated by (conversion of MA × target DP_{MA} × MW_{MA}) + (conversion of DOT × target DP_{DOT} × MW_{DOT}) + MW_{CDTPA}. (d) Molecular weight ($M_{n,app}$) and dispersity ($Đ$) were determined by SEC analysis (THF as eluent). (e) Without RAFT agent. (f) $OEOA_{480}$ was used as monomer. Molecular weight ($M_{n,app}$) and dispersity ($Đ$) were determined by SEC analysis (DMF as eluent). (g) CPDAP was used as CTA and MMA was used as monomer.

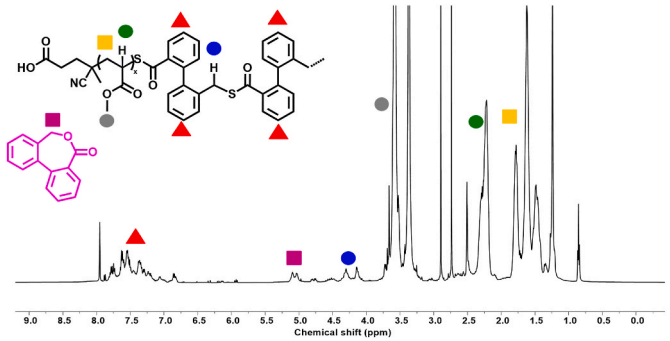

Fig. 3. ^{1}H NMR of PMA-*co*-P(DOT) (entry 2, Table 1) after purification in $CDCl_3$.

was synthesized and characterized by ^{1}H NMR and gas chromatography-mass spectrometry (GC-MS) according to the previous literatures (Figs. S1–S2) [28]. The polymerization of MA with different feed ratios of DOT (2.5 or 5 mol%) was carried out employing CDTPA as a chain transfer agent in dimethylformamide (DMF). After 24 h, the conversion of MA and thionolactone were 88 % and 95>%, respectively (entry 1, Table 1). The final conversions of MA were reduced with increasing the feed ratio of DOT (entry 2, Table 1). Furthermore, the experiment without DOT in the feed resulted in a faster polymerization rate and a narrower molecular weight distribution (entry 3, Table 1). This suggests the successful copolymerization of DOT and MA and agreed with previous literature where DOT acted as a retarder of the polymerization [27,28]. ^{1}H NMR of the purified copolymer (PMA-*co*-P(DOT)) shows the broadening of aromatic peaks as well as the appearance of new peaks at 4.1–4.3 ppm (Fig. 3), which were assigned to the methine groups adjacent to the thioester [35]. Notably, new peaks at 5.0–5.2 ppm in ^{1}H NMR and 170 ppm in ^{13}C NMR were also observed, which were not present in ^{1}H NMR of PMA-*co*-P(DOT) synthesized via FRP and AIBN initiated RAFT polymerization [27,28]. This peak was assigned to the desulfurization (dethionation)-oxidation side reaction of DOT in photo-induced conditions (*vide infra*) [36]. The ratio of the peaks for the side product at 5.0–5.2 ppm versus the thioester in the backbone at 4.1–4.3 ppm was 49 %, suggesting that nearly half of DOT was lost due to the side reactions. The control experiment without RAFT agent under the blue irradiation resulted in no conversion of MA (<5 %, entry 4, Table 1), excluding the possibility of direct radical generation from DOT in the presence of light. Nevertheless, it was observed that the yellow color of DOT completely faded, and its characteristic peaks at 5.15 and 5.45 ppm in ^{1}H NMR and 216 ppm in ^{13}C NMR disappeared, indicating the side reaction which led to the loss of thiocarbonyl group. The polymerization with a higher content of DOT was unsuccessful and led to the formation of polymers with significantly lower molecular weight ($M_{n,app}$) than theoretical molecular weight ($M_{n,the}$), as measured by SEC with poly(methyl methacrylate) (PMMA) standards. This was attributed to the increased extent of side reactions of MA and DOT that interfered with the polymerization (entry 5, Table 1). Also, the copolymerization of DOT with another acrylic monomer, oligo(ethylene oxide) methyl ether acrylate (average $M_n = 480$, $OEOA_{480}$) was feasible via PI RAFT polymerization (entry 6, Table 1; Fig. S3). This polymerization led to the formation of polymers with slightly higher dispersity ($Đ = 1.44$).

In all cases, polymers with monomodal size exclusion chromatography (SEC) traces and narrow molecular weight distributions were obtained (Fig. S4). We also noticed that $M_{n,app}$ of all polymers prepared with DOT were lower than the $M_{n,the}$ and also the control polymers without DOT. This further supports the successful incorporation of DOT into the copolymers, which may change the hydrodynamic volume of polymers, resulting in different elution time in SEC.

Photo-induced desulfurization-oxygenation of DOT. The loss of color in the polymerization of DOT and MA in the absence of a radical source underpins the susceptibility of thionolactone to undergo side reactions in photo-induced conditions. Interesting insights were obtained when model reactions of DOT and MA were performed in dimethyl sulfoxide (DMSO) under blue irradiation and analyzed by ^{1}H NMR, ^{13}C NMR, and GC-MS (Figs. S5–S7). Upon irradiation of DOT and MA in DMSO and disappearance of methine peaks adjacent to C=S (5.15 and 5.45 ppm in ^{1}H NMR and 216.0 ppm in ^{13}C NMR), new peaks appeared at 5.0–5.2 ppm in ^{1}H NMR and 170.0 ppm in ^{13}C NMR. The results revealed that DOT undergoes desulfurization-oxygenation and converts to the (oxo)lactone dibenzo [c,e]oxepin-5(7H)-one (Fig. 4A). Such desulfurization of DOT was reported in the previous literature during ATRP and was catalyzed by copper (I) complexes [36]. Additionally, desulfurization of other thiocarbonyl derivatives was observed in photo-induced conditions employing photocatalyst (*i.e.*, eosin y (EY) and chlorophyl) in the presence of ambient oxygen [66,67]. Nevertheless, DOT can undergo desulfurization-oxygenation in deoxygenated conditions and the absence of photocatalysts via reaction with MA while it remained nearly stable in DMSO alone.

We first speculated that water traces in the polymerization media are the possible oxygen source for desulfurization of DOT, but the photo-irradiation of DOT in the mixture of water and DMSO (1/1 *v/v*) resulted in formation of mostly the O–S isomerization product [68], the thiolactone dibenzo [c,e]thiepin-5(7H)-one (Figs. S8–S10). Although the mechanism of desulfurization-oxidation of DOT is still unclear and is not

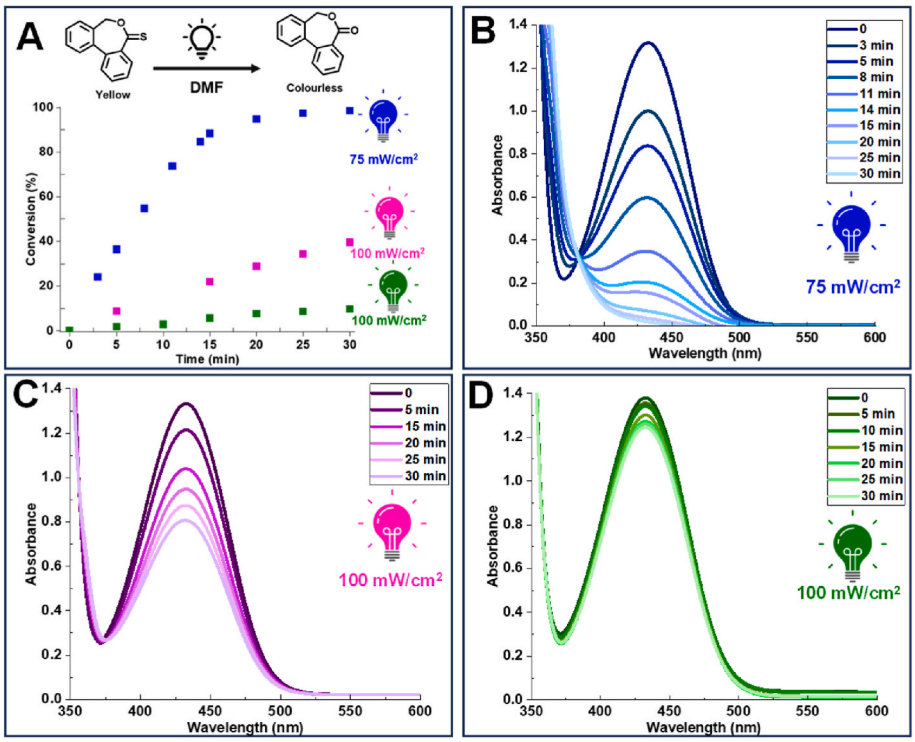

Fig. 4. Conversion of DOT to (oxo)lactone upon light irradiation after deoxygenation by N_2 sparging. The UV-VIS was measured at 3.5 mM of DOT in DMF and conversions of n→π* at 434 nm were used for calculating the conversions.

the focus of this study, it is known that photo-excited thiocarbonyls react with acrylates and form 4- and 5-membered thioether rings via 2-2 cycloaddition (Scheme S1), suggesting that monomers could be the source of oxygen for this reaction [69,70].

The effect of solvent on the desulfurization-oxygenation of DOT was also investigated using DMF, a typical solvent for the copolymerization of DOT. We found that DOT can undergo side reactions in DMF even in the absence of MA, possibly because DMF can act as a reagent in some organic reactions too [71]. To get further insight into the effect of light on the desulfurization of DOT in DMF, we monitored the kinetics of DOT n→π* absorption reduction upon irradiation with UV, blue, and green irradiation. As illustrated in Fig. 4, the irradiation with blue light yielded the fastest decrease of absorbance of C═S of DOT, whereas the UV irradiation resulted in *ca.* 3-Fold lower effects, albeit a UV light source with higher intensity was used. Expectedly, the irradiation with green light caused a negligible change in absorption, as there is very little overlap of absorption of DOT with the emission of green light source (Fig. 2). Collectively, these results suggest the extent of desulfurization of DOT follows the increasing order of blue > UV > green. The effect of two other solvents, namely anisole and toluene, in the photo-induced side reaction of DOT was investigated. Both solvents were previously used for RROP of DOT [35,38]. The results revealed that the loss of yellow color upon blue light irradiation, which indicates the side reaction, could not be prevented even in these non-polar solvents (Fig. S11). Also, it was observed that the extent of conversion correlates with the concentration of DOT, as the kinetics of conversion to (oxo)lactone plummeted when a higher concentration of DOT was irradiated with blue light.

PI RAFT copolymerization of DOT and MA with UV and green light. Challenges surrounding the side reaction of DOT upon irradiation with blue light may result in a significant loss of intact DOT for incorporation into the polymer's main chain. The higher molar absorptivity of DOT versus CDTPA suggests that DOT absorbs more photons and may undergo side reactions more rapidly than CDTPA to generate radicals to react with DOT. Indeed, the kinetics of polymerization of MA in the presence of DOT indicated that >95 % of the DOT is consumed in 7 h (incorporated into the polymers or converted to (oxo)lactone), while only 19 % of MA formed polymers.

Given the less pronounced effects of UV light on DOT desulfurization, we explored the photo-induced RROP of DOT and MA upon UV irradiation. The copolymerization afforded polymers with broader molecular weight distribution ($Đ$ = 1.67; entry 7, Table 1) and slower polymerization rate (95 % conversion in 45 h), although the molar absorption of CDTPA was much higher in the UV region versus the blue region, and UV light source with higher intensity (100 mW/Cm^2) was used for the polymerization. This observation is explained by the smaller overlap of UV light source emission with the absorption of CDTPA (Fig. 2), and the improved radical generation of trithiocarbonates upon excitation of n→π* transition (blue light region) versus π→π* (UV region) [72]. ^{1}H NMR analysis of the polymers prepared after UV irradiation indicated that the peaks of the (oxo)lactone were still present. It was concluded that although the desulfurization of DOT is much slower with UV irradiation, the slower polymerization time results in longer exposure of light to DOT which eventually results in a similar outcome as blue light.

The reduced extent of DOT desulfurization under green light irradiation renders it as the best light source for photo-RROP of DOT. Thus, we investigated the copolymerization of MA and DOT using another RAFT agent, the dithioester 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPDAP), because the photoactivation of CDTPA by green light did not occur (entry 8, Table 1) [47]. The extension of copolymerization of MA and DOT to green light employing CPDAP was also not possible, and no polymerization of MA happened in DMF after green light irradiation. This is because the dithioesters are typically considered inefficient RAFT agents for the polymerization of acrylates [73]. Replacing MA with methyl methacrylate (MMA), however, afforded 58 % and >95 % conversion of MMA and DOT by green light, but no DOT incorporation into the main chain was found (entry 9, Table 1). This is congruent with the previous works where DOT was reported to be a bystander in the copolymerization with MMA in thermal RAFT polymerization [27].

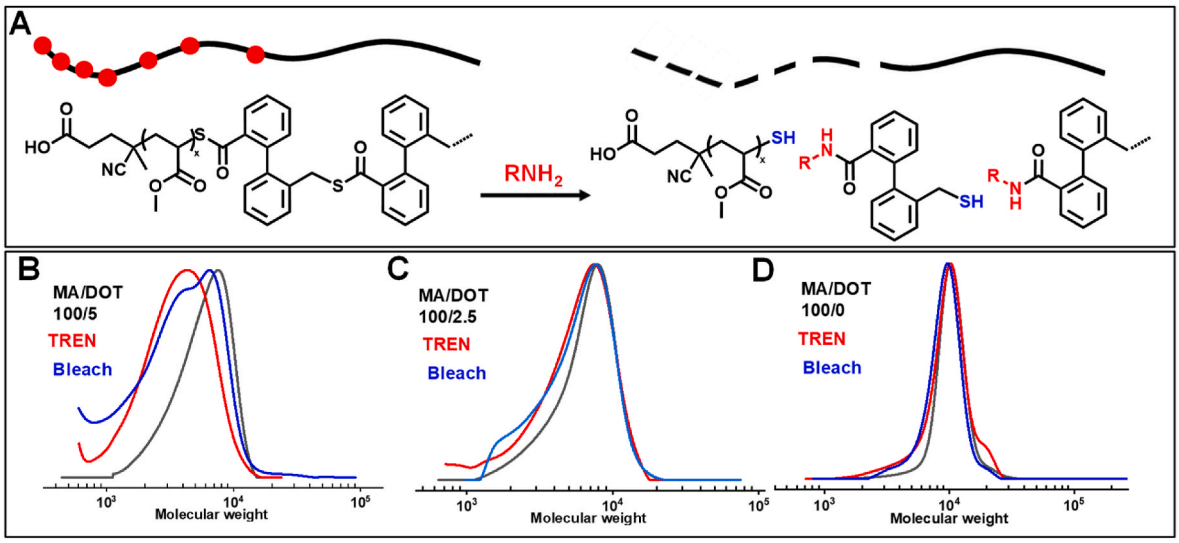

Fig. 5. Degradation of PMA-*co*-P(DOT) for entry 1, 2 and 3 in Table 1 after treatment with amines and bleach.

Our other attempts to extend photo-RROP of DOT to green light by employing PET RAFT polymerization with EY as photocatalyst were also unsuccessful, as EY rapidly photobleached in the presence of DOT upon light irradiation (Fig. S12).

Degradation of PMA-*co*-P(DOT) copolymers. Notwithstanding the side reactions of DOT in the photo-excited conditions, some DOT inserted into PMA backbones and formed thioester linkages that degraded under aminolysis or oxidation. The representative copolymers with 2.5 % and 5 % (entries 1 and 2 in Table 1) were treated with a primary amine source (tris(2-aminoethyl)amine, TREN) or bleach and analyzed by SEC after 25 h. In the presence of amines, the thioester cleaves to form thiol ends polymers (Fig. 5A), whereas bleach cleaves the thioester and forms several sulfur species in different oxidation states (*i.e.*, thiol, sulfoxide, sulfone, disulfide, and sulfonic acid). Both tested polymers disintegrated into polymers with low molecular weights (Fig. 5B and C); however, the most remarkable degradation was observed with the polymers having higher DOT contents. Given the higher reactivity of DOT compared to MA and gradient incorporation of the thioesters at the polymer head, the copolymers did not degrade to very small size fragments that correspond to the statistical distribution of thioester in the backbone. The control polymers almost remained intact under analogous conditions except for a minor broadening in the SEC trace which is attributed to the reaction of amines with ester side chains.

3. Conclusion

The RROP of the thionolactone DOT and MA was mediated by visible light irradiation using PI RAFT polymerization, yielding polyacrylates with thioester linkages in the backbone. In parallel to the RROP of DOT, photoexcitation of the thionolactone induced unwanted reactions and formed side products such as (oxo)lactone via desulfurization-oxygenation and O–S isomerization in the presence of water. Although the side reactions could be detrimental to the copolymerization due to the transformation of reactive thiocarbonyl to inert (oxo)lactone, some DOT was incorporated into the backbone and generated main chain degradable vinyl polymers that underwent main chain scission under both oxidation and aminolysis.

CRediT authorship contribution statement

Arman Moini Jazani: Writing – review & editing, Writing – original draft, Conceptualization. **Roksana Bernat:** Formal analysis. **Krzysztof Matyjaszewski:** Writing – review & editing, Writing – original draft, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: K Matyjaszewski reports a relationship with National Science Foundation that includes: funding grants. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2024.127032.

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