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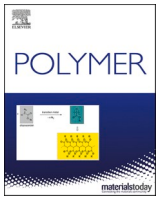

From health supplement to versatile monomer: Radical ring-opening polymerization and depolymerization of α-lipoic acid

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A B S T R A C T

The radical ring-opening polymerization (rROP) of α-lipoic acid (LA) and its derivatives represents a synthetically accessible, efficient, and scalable strategy to impart degradability into functional copolymers. This review highlights recent advances in the design of sustainable materials containing LA through rROP driven by heat and/or light.

1. Introduction

Developing synthetic strategies that yield degradable materials is an integral part of worldwide efforts to improve sustainability in the 21st century. A prime example is the synthesis of polymers such as polyesters [1,2] and related derivatives [3,4] that contain cleavable functional groups along the backbone, which facilitate, for example, recycling or degradation into innocuous byproducts in the natural environment. Unfortunately, the vast majority of commercially relevant polymeric materials—for example, produced by polymerization of vinyl monomers—are based on different chemistry (i.e., radical propagation) that makes incorporating degradable motifs significantly more challenging.

To address this opportunity, radical ring-opening polymerization (rROP) has enabled incorporation of degradable units along otherwise intractable polymeric backbones [5–15]. The basis of rROP is the design of cyclic comonomers that contain a degradable functional group as well as one that ring-opens under radical conditions and copolymerizes with conventional vinyl monomers. There are several classes of these special comonomers — such as macrocyclic allyl sulfides (MAS) [16–20], cyclic ketene acetals (CKA) [5,7–9,21–24], and dibenzo[c,e]-oxepane-5-thiones (DOT) [25–30] — that present exciting opportunities to design degradable materials. However, a challenge with all of the systems mentioned above is the need for multi-step synthesis to prepare the cyclic comonomers. In addition, there can be issues with monomer stability and reactivity that often complicate their use in practice.

This review focuses on a different, emerging building block for rROP with largely untapped potential: α-lipoic acid (LA). LA has a number of advantages that make it an attractive choice for the synthesis of degradable materials via rROP — it is bioderived, biocompatible, and commercially available on large scales (e.g., kilograms) in pure form as a supplement from popular consumer outlets such as Amazon.com [31] for pennies per gram. The ability of LA to participate in rROP relates to the disulfide bond contained in its saturated 1,2-dithiolane ring. This key dithiolane motif undergoes homolytic scission in the presence of heat, UV light, or radicals. Under the right conditions, ring-opened thiyl radicals will react with other dithiolanes to yield linear chains that also contain disulfide bonds in the backbone. Importantly, the chemical reactivity afforded by the cyclic disulfides can also be exploited to promote reactions with the disulfides created along the backbone in the polymeric materials. Indeed, the moderate bond energy (60 kcal mol^{-1}) of disulfide linkages is readily susceptible to dynamic exchange or cleavage in the presence of external stimuli (e.g., heat, light, radicals, nucleophiles) [32,33]. These factors have contributed to growing interest in 1,2-dithiolanes for use in a range of contemporary applications such as elastomers [34–36], self-healing materials [34–39], and chemical recycling [40–46].

Here, our goal is to highlight the reactivity of LA (Fig. 1) in radical-based polymerization reactions and discuss the exciting potential of this versatile molecular building block (Fig. 2). Readers interested in the

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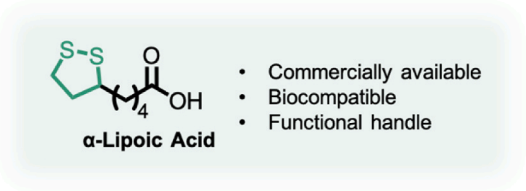

Fig. 1. α-Lipoic acid as a commercially available building block for synthesizing degradable polymers via radical ring-opening polymerization.

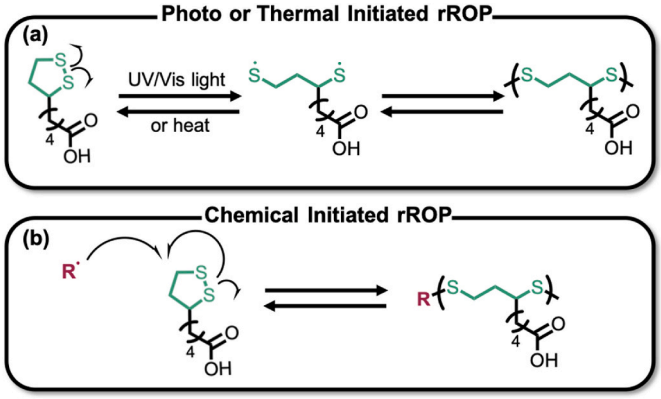

Fig. 2. α-Lipoic acid can undergo radical ring-opening polymerization in the presence of (a) light or heat and (b) a chemical initiator.

reactivity of LA under other complementary mechanisms such as anionic or cationic polymerization are referred to excellent recent literature [47–51].

2. Photoinitiated rROP

Photoinitiated polymerizations and crosslinking provide opportunities in 3D printing, advanced patterning, and functional coating systems [52–54]. Traditional formulations require the addition of photoinitiator(s), which can cause challenges in premature aging and discoloration. In contrast, the strained dithiolane ring present in LA homolytically cleaves to yield thiyl radicals in the presence of UV light without an additional radical initiator, providing an opportunity to simplify the formulation of materials [55–57]. The first dithiolane photopolymerization was reported by Barltrop et al. [56] where they irradiated trimethylene disulfide at −196 °C to preserve the build-up of thiyl radicals — upon heating, the radical species rapidly formed polymer. Further investigations were performed by Shi et al. by inducing polymerization of LA under visible light (420 nm) [37]. UV–vis analysis revealed that room-temperature depolymerization occurred by a radical mechanism induced by heat (T = 120 °C) but the reaction could be pushed to completion with subsequent UV irradiation (Fig. 3). Backbiting of the active thiyl radical chain end facilitates depolymerization back to LA monomer upon cooling to room temperature. When irradiated with visible light the reaction is pushed to completion and forms poly(catenanes) which lack radical chain ends due to their cyclic topology. These resulting poly(catenane) structures displayed excellent mechanical strength (E = 46.3 MPa) and thermal properties (T_g = 13 °C, T_{d5} = 307 °C) owing to the compacted cyclic topology of the polymer network. Closed-loop recyclability of the disulfide-containing backbone was demonstrated through radical depolymerization back to the starting LA monomer with UV light or thermal energy.

Sieredzinska et al. harnessed the inherent photo-responsivity of dithiolanes by introducing LA to a pendant amine on a polydimethylsiloxane (PDMS) backbone [45]. After 20 min of irradiation with a 365 nm UV lamp, complete crosslinking was achieved in the

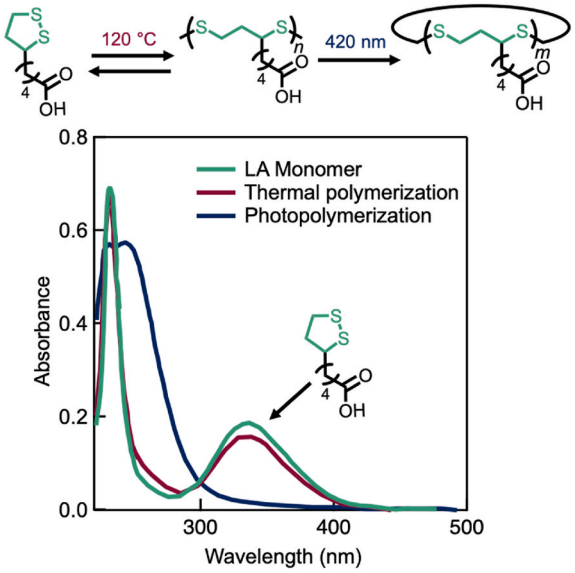

Fig. 3. *In-situ* photopolymerization drives polymerization to completion while thermal-induced rROP results in partial depolymerization of LA upon cooling to room temperature.

absence of solvent as confirmed by UV–vis spectroscopy through the disappearance of the 1,2-dithiolane absorption at 330 nm. Irradiation of the polymer in dilute solutions, also monitored by UV–vis spectroscopy confirmed a photo-induced radical mechanism based on the distinctive thiyl absorption observed at 500 nm. After cross-linking, the networks swelled as expected and could be transformed back into their linear precursors with a thiolate initiator due to the presence of dynamic disulfide crosslinks. Similarly, Choi et al. designed networks from LA-terminated PDMS macromonomers to develop super-soft bottlebrush elastomers with a LA-constructed backbone [34]. Synthetically, in contrast to lipoic acid as a small molecule, the PDMS-LA macromonomers did not ring open thermally but were still efficiently activated with UV light (365 nm) to yield photocurable bottlebrush networks. The dynamic nature of the S–S backbone created an opportunity for reprocessable and self-healable materials through heat or UV light as an external stimulus (Fig. 4). Furthermore, the elastomers degraded thermally (>180 °C) and chemically through basic (sodium hydroxide) or reductive conditions (sodium borohydride).

Furthermore, the Anseth group leveraged biocompatible LA as a versatile platform to produce dynamic disulfide crosslinks in poly (ethylene glycol)–lipoic acid (PEG-LA) hydrogel networks for cell encapsulation through UV (365 nm) light-induced rROP [58]. Asparagusic acid (AA) was used as an alternate 1,2-dithiolane for comparison, but both LA and AA displayed similar curing kinetics, plateau moduli, and absorbance such that LA was used as a model dithiolane for further studies. In the presence of protic solvents, the photoinitiator-free PEG-LA system produced linear disulfide crosslinks and one unreacted thiol (per dithiolane ring) that quickly undergoes a hydrogen atom transfer in the presence of a protic solvent molecule, resulting in a pendant thiol (Fig. 5). Networks were also constructed from tetra-PEG-norbornene (Nb) and tetra-PEG-LA in the presence of a photoinitiator, resulting in longer kinetic chain lengths as compared to those formed from only tera-PEG-LA. No reaction was observed between PEG-LA and PEG-Nb in the absence of a photoinitiator, even high energy UV irradiation (100 mW cm^{-2}, >10 min). Hydrogel networks with disulfide crosslinks underwent passive and photoinduced stress relaxation that could be controlled through the addition of Nb, thiols, or photoinitiators. The subsequent radical-mediated photodegradation of PEG-LA hydrogel networks occurred from radical scission of the disulfide crosslinks as initiated by irradiation with 365 nm light for up to 60 s.

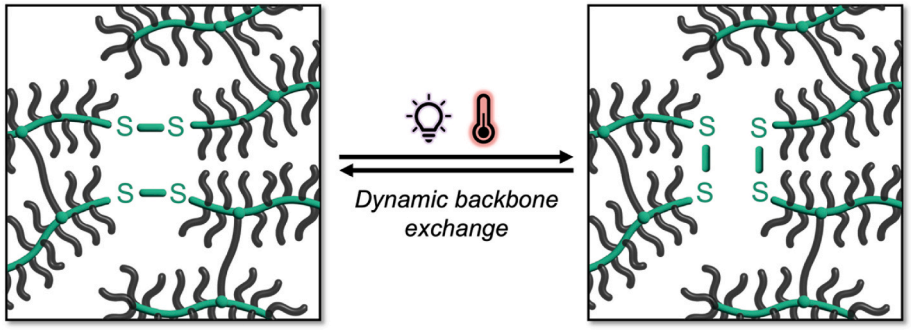

Fig. 4. Dynamic exchange of disulfide bonds along the bottlebrush backbone enables self-healing and reprocessing under UV light or heat.

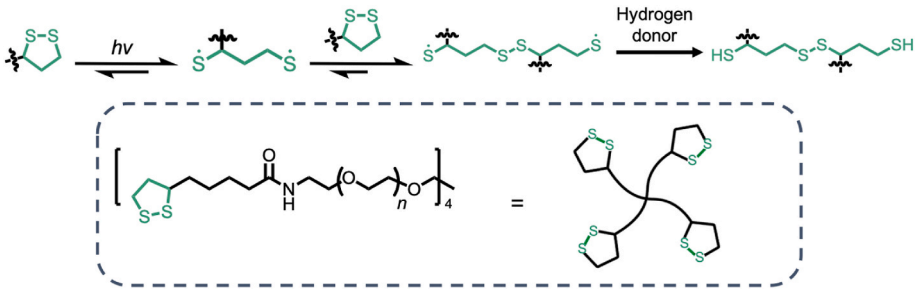

Fig. 5. Dithiolane photocrosslinking mechanism for hydrogel networks. In the presence of protic solvents, rapid hydrogen transfer occurs with the thiyl radical resulting in a pendant thiol chain end.

However, networks formed from PEG-Nb and PEG-LA formed thioether crosslinks that are not susceptible to radical-induced bond cleavage.

Choi et al. designed a resin for 3D printing containing a LA macromonomer and diacrylate that copolymerize under 385 nm light irradiation to form 3D printed bottlebrush networks [42]. With this application in mind, the kinetics of rROP were crucial to obtain rapid layer-by-layer printing, which benefited from the addition of phenylbis (2,4,6-trimethylbenzoyl)phosphine oxide (BAPO) as a photoinitiator. Printed objects exhibited self-healing properties through the dynamic exchange of disulfides either thermally or in the presence of base at room temperature. Recently, Shi et al. synthesized supramolecular poly (disulfide) networks via photoinduced rROP in the molten state from LA modified with an electron-rich oligopeptide for dynamically tunable emissive systems [59]. They elegantly demonstrated the recycling pathways through reconfiguration mediated by disulfide bond exchange or chemical recycling from thiol-induced depolymerization of polymer back to monomer.

3. Thermally initiated rROP

Due to the limits of light penetration, thermally initiated polymerizations are an attractive approach to achieve large batches and high molecular weight polymers [60]. This prompted an investigation of the thermal initiation of 1,2-dithiane (DT) by Endo in 2004 in an effort to synthesize polymers with cyclic topologies [61,62]. They found the polymerization proceeds efficiently above the melting temperature of the dithiolane [63] ($T_m = 70$ °C) and was quantitatively quenched with the addition of benzyl mercaptan. In the presence of butanedithiol (BDT), molecular weight was suppressed, but ^{1}H NMR revealed a polymer with resonances consistent with thiol chain ends. Poly(DT) in the absence of extraneous thiols lacked these characteristic thiol resonances suggesting the polymerization resulted in a polymer with a cyclic topology. Additional studies showed the cyclic polymer converted to a linear topology with thiol chain ends after UV irradiation and the addition of a reducing agent. Similarly, intramolecular oxidation of the linear poly(DT-BDT) converted the linear polymer to the cyclic topology with triethylamine and iodine. Endo extended these studies by thermally polymerizing poly(LA-DT) copolymers in the melt, noting the reaction only proceeds above the melting temperature of both dithiolane species [64]. The resulting copolymers were topologically linked poly(catenane) structures incorporating both comonomers in the backbone with a higher incorporation of LA attributed to the increased ring strain of the monomer (Fig. 6).

Pioneering work by the Tian group investigated the thermally induced rROP of LA and noticed, upon cooling, the ring-closing depolymerization of oligomers beginning at the terminal thiyl radicals [35,65]. This metastability was overcome by quenching the terminal radicals with 1,3-diisopropenylbenzene (DIB, 20 wt%). Supramolecular networks could be synthesized on multigram scales by heating all three components to 70 °C followed by slowly cooling to room temperature. Thermal properties were tailored with the addition of iron(III) ions that toughen the resulting materials through coordination with pendant carboxylic acid groups on LA to yield networks with glass transition temperatures ranging from −20 °C to 105 °C. Outstanding elongation was attributed to dynamic disulfide bonds, hydrogens bonds, and coordinative bonds with iron(III) leading to energy dissipation during stretching. In addition, exceptional mechanical strength was attributed to a high crosslink density and iron(III) incorporation [66]. This process

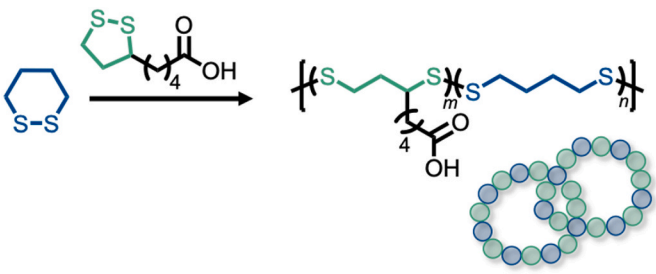

Fig. 6. Mechanism of thermally induced radical ring-opening copolymerization of dithiane and lipoic acid reportedly results in poly(catenanes).

yielded tough elastomers with dynamic self-healing character at room temperature in the absence of external stimuli. Though the kinetics of the disulfide exchange occurred on longer time scales, self-healing was rapid due to weaker iron(III) coordination bonds. This motivated Deng et al. to design networks with a similar molecular composition but higher loadings of iron(III) in an effort to make low-cost, high--performance dynamic composites [36]. Higher temperatures (T = 150 °C) were necessary for processability and upon cooling, the yellow molten mixture turned brown, signifying the formation of iron clusters within the polymer network [67]. With higher iron(III) content, dramatic changes were observed in Young's modulus (E = 0.09 MPa → 7.8 MPa) and tensile strength (U_T = 0.05 MPa → 1.9 MPa). However, increased iron(III) loadings led to networks with poor self-healing characteristics, a consequence of the slow dynamics from the build-up of iron clusters. Curiously, the resulting networks also exhibited humidity resistance despite the significant concentration of ionic bonds. To further exploit dithiolane dynamics and facilitate recycling, Zhang et al. omitted DIB as a static crosslink from the formulation. The addition of metal ions (Fe^{3+}, Cu^{2+}, Zn^{2+}, and Ca^{2+}) while LA was in the melt stabilized the networks without the addition of covalent crosslinks (e.g., DIB) [44]. Supramolecular networks could be depolymerized under basic conditions (e.g., NaOH) and LA monomer retrieved in high yield (~80 %) through precipitation with HCl (pH = 3–4) and immediate extraction into an organic solvent (Fig. 7). This innovative recycling process was demonstrated through large-scale (~100 g) depolymerizations and multiple chemical recycling and reprocessing cycles with nearly identical properties to the original LA network being observed for the recycled systems. A key issue in recycled polymers is the influence of accumulated fatigue on mechanical performance rendering the material no longer functional. These authors demonstrated that LA-based polymers circumvented this issue through both physical and chemical recycling processes. With a network comprised entirely of dynamic supramolecular crosslinks (i.e., no static crosslinks), poly(LA-Fe) was able to completely self-heal with almost identical stiffness and elongation. In addition, polymer networks reformed from chemically recycled LA monomer fully recovered their mechanical performance for up to three polymerization–depolymerization cycles.

Recently, Zheng et al. designed silicone bottlebrush networks for thermally conductive materials leveraging LA as a dynamic backbone for reprocessing [68]. Monofunctional PDMS-LA was heated to 120 °C to initiate rROP and after 4 h, the polymerization reached equilibrium around 51 % monomer conversion. The authors reported no increase in conversion at temperatures >120 °C due to the reversible nature of LA at elevated temperatures. PDMS-LA bottlebrush networks could then be remolded at elevated temperatures (>190 °C, 30 MPa) displaying identical mechanical properties as the pristine polymer.

4. Chemically initiated rROP

The addition of a chemical initiator has further expanded the synthetic toolbox for developing dynamic and degradable materials with LA and its derivatives. Introducing other vinyl monomers significantly expands the scope of accessible physical properties with dithiolane-based polymers. Endo first explored the copolymerization of lipoamide (LAm) with a range of vinyl comonomers such as styrene (S), vinyl acetate (VA), methyl acrylate (MA), methyl methacrylate (MMA), and acrylonitrile (AN) in the presence of 2,2′-azobis(isobutyronitri1e) (AIBN) as a thermal initiator [69]. They observed that MMA did not copolymerize with LAm and attributed the lack of reactivity to steric crowding of MMA–LAm diads. The other copolymerizations were successful with a yield and kinetics that were found to depend on comonomer reactivity (MA > AN > VA > S).

Tsarevsky and coworkers drew further inspiration from lipoate moieties used in a variety of applications such as dental adhesives [70,71], surface modifiers [72,73], and quantum dots [74]. They first started with the copolymerization of ethyl lipoate (ELp) and ethyl acrylate (1:1) to investigate disulfide formation during polymerization that imparts degradability in linear copolymers [75]. The addition of a strong reducing agent, tri-*n*-butylphosphine (Bu_3P), promoted a significant reduction in molecular weight compared to the original copolymers owing to the high concentration of disulfides formed along the backbone. These findings led them to design a difunctional monomer, 2-acryloyloxyethyl lipoate (AELp), that forms highly branched structures capable of degradation through disulfide reduction. Polymerization of AELp could be initiated with AIBN at 65 °C and the reaction intentionally stopped prior to gelation (~20 % monomer conversion). The resulting highly branched polymers were probed for degradability with several disulfide-reducing agents. Bu_3P again showed optimal reactivity toward disulfides while dithiothreitol (DTT) was found to reduce backbone disulfides but also react with pendant acrylate groups through thiol–ene addition, producing polymers with higher molecular weights (Fig. 8).

Building on their previous work, Tsarevsky sought to explore the kinetics and thermodynamics of lipoate rROP and depolymerization. The reversibility of ELp polymerization was realized from the conversion plateau observed at various temperatures (40 °C, 70 °C, 90 °C and 105 °C) — attributed to the existence of a ceiling temperature (T_c = 139 °C) [76]. It was noted that altering the polymerization conditions to higher temperatures and lower concentrations decreased the conversion plateau which is expected based on the kinetics of thermal rROP of dithiolanes [62]. The thermal depolymerization of poly(ethyl lipoate) (PELp) was performed at 150 °C, above the T_c, further supporting the reversibility of disulfide formation. At elevated temperatures, homolytic cleavage of the disulfide bonds generates radicals necessary for depolymerization, but it was also shown that depolymerization could occur at lower temperatures with a chemical initiator (Fig. 9). This

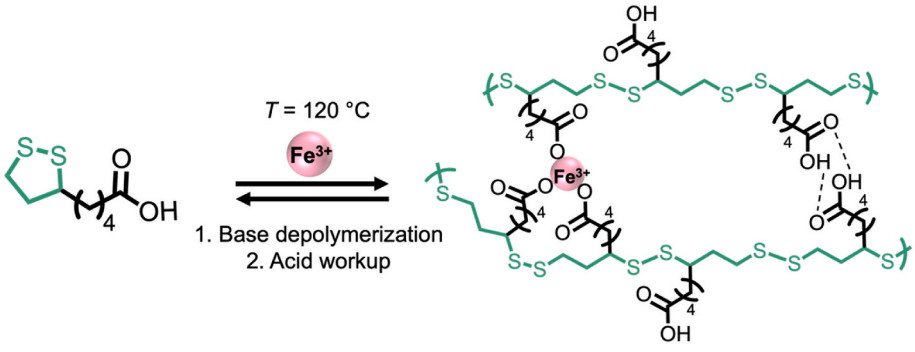

Fig. 7. Tough and elastic LA supramolecular networks can be formed in the presence of a metal salt such as $FeCl_3$. LA monomer can also be recovered through base-mediated depolymerization and isolated after an acid workup.

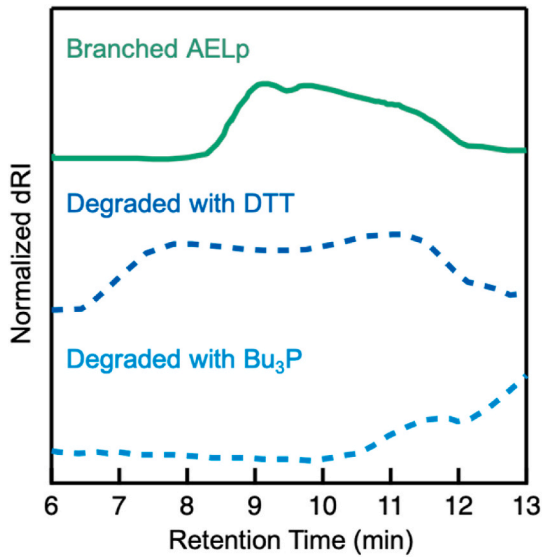

Fig. 8. SEC traces of highly branched AELp (top) and corresponding degradation products with DTT (middle) and Bu_3P (bottom).

groundbreaking work inspired our group to investigate the copolymerization of ELp with vinyl monomers for high-performance pressure-sensitive adhesives [41]. A mechanistic study was conducted with ELp and *n*-butyl acrylate (*n*BA) to reveal that diad sequence and degradability strongly depend on the reaction conditions used during copolymerization. It was found that the copolymerization of ELp with *n*BA exhibits reversibility in the propagation of 1,2-dithiolane monomer, where higher monomer concentrations ([M]) and lower temperatures (*T*) favor the formation of ELp–ELp units that contain degradable disulfide bonds (Fig. 10). Copolymers synthesized at low *T* and high [M] had more disulfides along the backbone and thus degraded to lower molecular weight oligomers (e.g., M_n = 198 kg mol^{-1} → 2.6 kg mol^{-1}) upon exposure to mild reducing agents such as tris(2-carboxyethyl) phosphine) (TCEP) as a mild reducing agent. In contrast, copolymers synthesized at high *T* and low [M] had fewer disulfides along the backbone, degrading to higher molecular weight oligomers (M_n = 175 kg mol^{-1} → 13 kg mol^{-1}). The thiol chain ends produced after degradation were oxidatively repolymerized (e.g., M_n = 13 kg mol^{-1} → 142 kg mol^{-1}) with I_2 and pyridine to demonstrate the opportunity for closed-loop recycling.

5. Controlled rROP

Several detailed examples were recently reported on controlled polymerizations involving ring-opening of lipoic acid derivatives [47,49,51,77–79]. However, only one known example exists pertaining to rROP of LA which was recently reported by our group using addition–fragmentation chain-transfer polymerization (RAFT) (Fig. 11a) [40]. The potential sulfur chelation of LA to metal catalysts limits the use of other techniques such as atom-transfer radical polymerization (ATRP) and ring-opening metatheses polymerizations (ROMP). RAFT conditions were used to synthesize copolymers with up to 30 % LA in the feed (Fig. 11b), producing low molar-mass dispersities ($Đ$ = 1.12–1.25) as well as excellent chain-end fidelity that enabled reinitiation and block copolymer formation. LA also smoothly and controllably copolymerizes with a variety of functional acrylate derivatives and acrylamides to yield materials with a range of physical properties. However, the radical stability of lipoic acid was not compatible with styrene and methyl methacrylate and resulted in homopolymerization of each respective vinyl monomer. Copolymer degradation proceeded readily through the reduction of disulfide bonds with TCEP and $NaBH_4$. Notably, degradation of thioethers with $AgNO_3$ resulted in oligomers with even lower molar masses [14,80].

6. Conclusions and future outlook

Throughout this perspective, we outlined the various methods for radical ring-opening polymerization of α-lipoic acid and its derivatives. The use of LA as a commercially available monomer has allowed the rapid discovery of degradable and dynamic materials initiated by UV light, heat, and/or a chemical additive. Despite these quality achievements, several challenges and opportunities still exist in harnessing the full potential of LA as a building block in advanced materials. We conclude this review with brief remarks detailing potential areas of future exploration and coinciding challenges.

One sought-after application for degradable materials is designing sustainable plastics and rubbers. However, the inherently low glass-transition temperature of LA (T_g = −10 °C) and its derivatives has limited the application of LA polymers. The labile nature of the LA backbone and side chain suggest the exploration of alternate 1,2-dithiolanes may prove to be a more promising route. The Sumerlin group has shown encouraging results relating to the synthesis and characterization of functionalized 1,2-dithiolanes that hold promise in rROP among other applications [81,82]. However, the synthesis of these monomers can be complex, requiring multiple steps. Simplifying and optimizing the

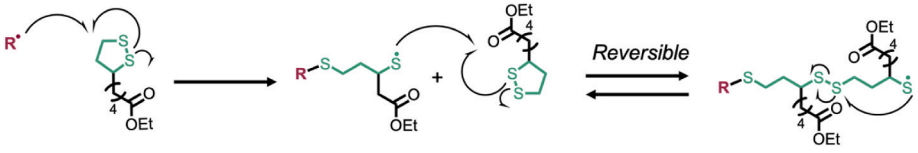

Fig. 9. Mechanism of reversible propagation in radical-mediated polymerizations of ethyl lipoate.

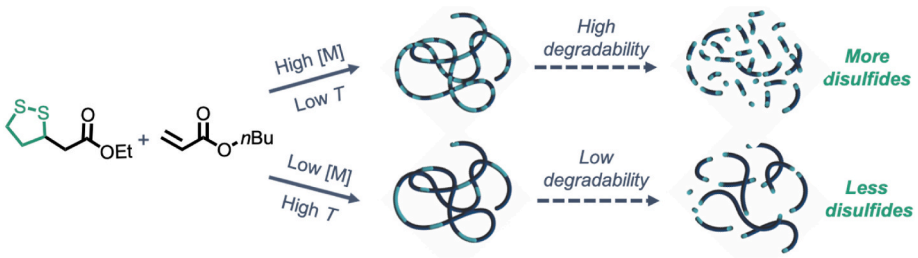

Fig. 10. Tunable degradation of poly(acrylates) as recyclable materials. The degradability of lipoic-acid–acrylate copolymers can be synthetically tuned through polymerization conditions that control the average number of disulfide bonds per polymer chain. [M] represents the total monomer concentration.

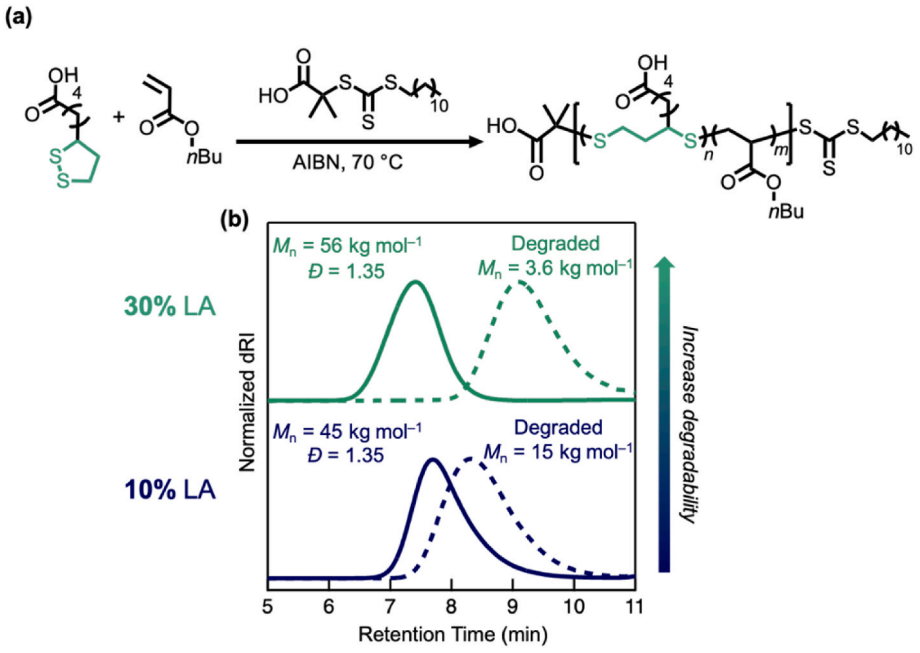

Fig. 11. Controlled copolymerization of poly(butyl acrylate-*co*-lipoic acid) via RAFT. **(a)** synthesis of *n*BA-LA. **(b)** SEC analysis depicts the control over degradability based on LA feed.

synthetic methods is essential for scalability and practicality. Also, it is important to remember that LA–LA diad formation is crucial to forming degradable disulfide bonds, and with new monomers comes different copolymerization kinetics and thermodynamics that will need to be understood for full control over sequence and properties.

The recent discovery of controlled rROP of LA was an important addition to our collective synthetic toolbox, but the limitation of compatible comonomers (i.e., only acrylates and acrylamides) leaves space to be explored. In addition, finding methods to control the stereoregularity may prove powerful for synthesizing more robust materials with a broader range of material properties. Finally, the trade-off between dynamic and degradable is also a significant consideration with LA-based polymers. Though degradable, S–S bonds possess dynamic functionality in the presence of heat, light, and base, which potentially limits the thermomechanical robustness of LA-based materials [42, 83–86].

In summary, LA holds considerable promise as a naturally occurring building block for designing degradable materials at scale. Harnessing its reactivity has just begun and we are excited for the broader community to unlock its full potential in radical ring-opening polymerizations and beyond.

CRediT authorship contribution statement

Kaitlin R. Albanese: Writing – review & editing, Writing – original draft. **Javier Read de Alaniz:** Writing – review & editing, Writing – original draft. **Craig J. Hawker:** Writing – review & editing, Writing – original draft, Conceptualization. **Christopher M. Bates:** Writing – review & editing, Writing – original draft.

Declaration of competing interest

The authors 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

No data was used for the research described in the article.

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References

[1] Q. Carboué, S. Fadlallah, M. Lopez, F. Allais, Progress in degradation behavior of most common types of functionalized polymers: a review, Macromol. Rapid Commun. 43 (13) (2022) 2200254, https://doi.org/10.1002/marc.202200254.
[2] M. Vert, Aliphatic polyesters: great degradable polymers that cannot do everything, Biomacromolecules 6 (2) (2005) 538–546, https://doi.org/10.1021/bm0494702.
[3] J. Yuan, W. Xiong, X. Zhou, Y. Zhang, D. Shi, Z. Li, H. Lu, 4-Hydroxyproline-Derived sustainable polythioesters: controlled ring-opening polymerization, complete recyclability, and facile functionalization, J. Am. Chem. Soc. 141 (12) (2019) 4928–4935, https://doi.org/10.1021/jacs.9b00031.
[4] H. Li, S.M. Guillaume, J. Carpentier, Polythioesters prepared by ring-opening polymerization of cyclic thioesters and related monomers, Chem. Asian J. 17 (17) (2022), https://doi.org/10.1002/asia.202200641.
[5] T. Pesenti, J. Nicolas, 100th anniversary of macromolecular science viewpoint: degradable polymers from radical ring-opening polymerization: latest advances, new directions, and ongoing challenges, ACS Macro Lett. 9 (12) (2020) 1812–1835, https://doi.org/10.1021/acsmacrolett.0c00676.
[6] A. Tardy, J. Nicolas, D. Gigmes, C. Lefay, Y. Guillaneuf, Radical ring-opening polymerization: scope, limitations, and application to (Bio)Degradable materials, Chem. Rev. 117 (3) (2017) 1319–1406, https://doi.org/10.1021/acs.chemrev.6b00319.
[7] A. Tardy, J.-C. Honoré, J. Tran, D. Siri, V. Delplace, I. Bataille, D. Letourneur, J. Perrier, C. Nicoletti, M. Maresca, C. Lefay, D. Gigmes, J. Nicolas, Y. Guillaneuf, Radical copolymerization of vinyl ethers and cyclic ketene acetals as a versatile platform to design functional polyesters, Angew. Chem. Int. Ed. 56 (52) (2017) 16515–16520, https://doi.org/10.1002/anie.201707043.
[8] A.W. Jackson, Reversible-deactivation radical polymerization of cyclic ketene acetals, Polym. Chem. 11 (21) (2020) 3525–3545, https://doi.org/10.1039/D0PY00446D.
[9] A.W. Jackson, S. Reddy Mothe, L.R. Chennamaneni, A. van Herk, P. Thoniyot, Unraveling the history and revisiting the synthesis of degradable polystyrene analogues via radical ring-opening copolymerization with cyclic ketene acetals, Materials 13 (10) (2020) 2325, https://doi.org/10.3390/ma13102325.
[10] W.J. Bailey, Z. Ni, S.R. Wu, Free radical ring-opening polymerization of 4,7-dimethyl-2-methylene-1,3-dioxepane and 5,6-benzo-2-methylene-1,3-dioxepane, Macromolecules 15 (3) (1982) 711–714, https://doi.org/10.1021/ma00231a006.
[11] W.J. Bailey, S.-R. Wu, Z. Ni, Synthesis and free radical ring-opening polymerization of 2-methylene-4-phenyl-1,3-dioxolane, Makromol. Chem. 183 (8) (1982) 1913–1920, https://doi.org/10.1002/macp.1982.021830811.

[12] S. Agarwal, Chemistry, chances and limitations of the radical ring-opening polymerization of cyclic ketene acetals for the synthesis of degradable polyesters, Polym. Chem. 1 (7) (2010) 953, https://doi.org/10.1039/c0py00040j.
[13] S. Agarwal, Chemistry, chances and limitations of the radical ring-opening polymerization of cyclic ketene acetals for the synthesis of degradable polyesters, Polym. Chem. 1 (7) (2010) 953, https://doi.org/10.1039/c0py00040j.
[14] H. Watanabe, M. Kamigaito, Direct radical copolymerizations of thioamides to generate vinyl polymers with degradable thioether bonds in the backbones, J. Am. Chem. Soc. 145 (20) (2023) 10948–10953, https://doi.org/10.1021/jacs.3c01796.
[15] A.M. Jazani, R. Bernat, K. Matyjaszewski, Visible light-induced photo-radical ring-opening copolymerization of thionolactone and acrylates, Polymer 302 (2024) 127032, https://doi.org/10.1016/j.polymer.2024.127032.
[16] W. Wang, B. Rondon, Z. Wang, J. Wang, J. Niu, Macrocyclic allylic sulfone as a universal comonomer in organocatalyzed photocontrolled radical copolymerization with vinyl monomers, Macromolecules 56 (5) (2023) 2052–2061, https://doi.org/10.1021/acs.macromol.2c02025.
[17] W. Wang, Z. Zhou, D. Sathe, X. Tang, S. Moran, J. Jin, F. Haeffner, J. Wang, J. Niu, Degradable vinyl random copolymers via photocontrolled radical ring-opening cascade copolymerization, Angew. Chem. Int. Ed. 61 (8) (2022), https://doi.org/10.1002/anie.202113302.
[18] R.A. Evans, E. Rizzardo, Free-radical ring-opening polymerization of cyclic allylic sulfides, Macromolecules 29 (22) (1996) 6983–6989, https://doi.org/10.1021/ma960573p.
[19] R.A. Evans, G. Moad, E. Rizzardo, S.H. Thang, New free-radical ring-opening acrylate monomers, Macromolecules 27 (26) (1994) 7935–7937, https://doi.org/10.1021/ma00104a062.
[20] J.M.J. Paulusse, R.J. Amir, R.A. Evans, C.J. Hawker, Free radical polymers with tunable and selective bio- and chemical degradability, J. Am. Chem. Soc. 131 (28) (2009) 9805–9812, https://doi.org/10.1021/ja903245p.
[21] N.-C. Jiang, Z. Zhou, J. Niu, Quantitative, regiospecific, and stereoselective radical ring-opening polymerization of monosaccharide cyclic ketene acetals, J. Am. Chem. Soc. 146 (8) (2024) 5056–5062, https://doi.org/10.1021/jacs.3c14244.
[22] B.A. Abel, R.L. Snyder, G.W. Coates, Chemically recyclable thermoplastics from reversible-deactivation polymerization of cyclic acetals, Science 373 (6556) (2021) 783–789, https://doi.org/10.1126/science.abh0626.
[23] Y. Du, Y. Du, S. Lazzari, T. Reimers, R. Konradi, T.W. Holcombe, E.B. Coughlin, Mechanistic investigation of cyclic ketene acetal radical ring-opening homo- and Co-polymerization and preparation of PEO graft copolymers with tunable composition, Polym. Chem. 13 (41) (2022) 5829–5840, https://doi.org/10.1039/D2PY00986B.
[24] M.R. Hill, E. Guégain, J. Tran, C.A. Figg, A.C. Turner, J. Nicolas, B.S. Sumerlin, Radical ring-opening copolymerization of cyclic ketene acetals and maleimides affords homogeneous incorporation of degradable units, ACS Macro Lett. 6 (10) (2017) 1071–1077, https://doi.org/10.1021/acsmacrolett.7b00572.
[25] M.F.I. Rix, K. Collins, S.J. Higgs, E.M. Dodd, S.J. Coles, N.M. Bingham, P.J. Roth, Insertion of degradable thioester linkages into styrene and methacrylate polymers: insights into the reactivity of thionolactones, Macromolecules 56 (23) (2023) 9787–9795, https://doi.org/10.1021/acs.macromol.3c01811.
[26] G.R. Kiel, D.J. Lundberg, E. Prince, K.E.L. Husted, A.M. Johnson, V. Lensch, S. Li, P. Shieh, J.A. Johnson, Cleavable comonomers for chemically recyclable polystyrene: a general approach to vinyl polymer circularity, J. Am. Chem. Soc. 144 (28) (2022) 12979–12988, https://doi.org/10.1021/jacs.2c05374.
[27] R.A. Smith, G. Fu, O. McAteer, M. Xu, W.R. Gutekunst, Radical approach to thioester-containing polymers, J. Am. Chem. Soc. 141 (4) (2019) 1446–1451, https://doi.org/10.1021/jacs.8b12154.
[28] N.M. Bingham, P.J. Roth, Degradable vinyl copolymers through thiocarbonyl addition–ring-opening (TARO) polymerization, Chem. Commun. 55 (1) (2019) 55–58, https://doi.org/10.1039/C8CC08287A.
[29] H. Elliss, F. Dawson, Q. un Nisa, N.M. Bingham, P.J. Roth, M. Kopeć, Fully degradable polyacrylate networks from conventional radical polymerization enabled by thionolactone addition, Macromolecules 55 (15) (2022) 6695–6702, https://doi.org/10.1021/acs.macromol.2c01140.
[30] N. Gil, B. Caron, D. Siri, J. Roche, S. Hadiouch, D. Khedaioui, S. Ranque, C. Cassagne, D. Montarnal, D. Gigmes, C. Lefay, Y. Guillaneuf, Degradable polystyrene via the cleavable comonomer approach, Macromolecules 55 (15) (2022) 6680–6694.
[31] Bulk Supplements Alpha Lipoic Acid. Amazon.com. https://a.co/d/7mZKZJn.
[32] A.G. Orrillo, R.L.E. Furlan, Sulfur in dynamic covalent chemistry, Angew. Chem. Int. Ed. 61 (26) (2022) e202201168, https://doi.org/10.1002/anie.202201168.
[33] A.W. Jackson, Reversible-deactivation radical polymerization of cyclic ketene acetals, Polym. Chem. 11 (21) (2020) 3525–3545, https://doi.org/10.1039/D0PY00446D.
[34] C. Choi, J.L. Self, Y. Okayama, A.E. Levi, M. Gerst, J.C. Speros, C.J. Hawker, J. Read de Alaniz, C.M. Bates, Light-mediated synthesis and reprocessing of dynamic bottlebrush elastomers under ambient conditions, J. Am. Chem. Soc. 143 (26) (2021) 9866–9871, https://doi.org/10.1021/jacs.1c03686.
[35] Q. Zhang, C.-Y. Shi, D.-H. Qu, Y.-T. Long, B.L. Feringa, H. Tian, Exploring a naturally tailored small molecule for stretchable, self-healing, and adhesive supramolecular polymers, Sci. Adv. 4 (7) (2018) eaat8192, https://doi.org/10.1126/sciadv.aat8192.
[36] Y. Deng, Q. Zhang, B.L. Feringa, H. Tian, D. Qu, Toughening a self-healable supramolecular polymer by ionic cluster-enhanced iron-carboxylate complexes, Angew. Chem. Int. Ed. 59 (13) (2020) 5278–5283, https://doi.org/10.1002/anie.201913893.
[37] C.-Y. Shi, Q. Zhang, B.-S. Wang, M. Chen, D.-H. Qu, Intrinsically photopolymerizable dynamic polymers derived from a natural small molecule, ACS Appl. Mater. Interfaces 13 (37) (2021) 44860–44867, https://doi.org/10.1021/acsami.1c11679.
[38] J. Zhu, S. Zhao, J. Luo, W. Niu, J.T. Damron, Z. Zhang, M.A. Rahman, M. A. Arnould, T. Saito, R. Advincula, A.P. Sokolov, B.G. Sumpter, P.-F. Cao, A novel dynamic polymer synthesis via chlorinated solvent quenched depolymerization, CCS Chem. (2022) 1–13, https://doi.org/10.31635/ccschem.022.202202362.
[39] Q. Zhang, Y.-X. Deng, H.-X. Luo, C.-Y. Shi, G.M. Geise, B.L. Feringa, H. Tian, D.-H. Qu, Assembling a natural small molecule into a supramolecular network with high structural order and dynamic functions, J. Am. Chem. Soc. 141 (32) (2019) 12804–12814, https://doi.org/10.1021/jacs.9b05740.
[40] K.R. Albanese, P.T. Morris, J. Read de Alaniz, C.M. Bates, C.J. Hawker, Controlled-radical polymerization of α-lipoic acid: a general route to degradable vinyl copolymers, J. Am. Chem. Soc. 145 (41) (2023) 22728–22734, https://doi.org/10.1021/jacs.3c08248.
[41] K.R. Albanese, Y. Okayama, P.T. Morris, M. Gerst, R. Gupta, J.C. Speros, C. J. Hawker, C. Choi, J. Read de Alaniz, C.M. Bates, Building tunable degradation into high-performance poly(acrylate) pressure-sensitive adhesives, ACS Macro Lett. 12 (6) (2023) 787–793, https://doi.org/10.1021/acsmacrolett.3c00204.
[42] C. Choi, Y. Okayama, P.T. Morris, L.L. Robinson, M. Gerst, J.C. Speros, C. J. Hawker, J. Read de Alaniz, C.M. Bates, Digital light processing of dynamic bottlebrush materials, Adv. Funct. Mater. 32 (25) (2022) 2200883, https://doi.org/10.1002/adfm.202200883.
[43] C.-Y. Shi, Q. Zhang, B.-S. Wang, D.-D. He, H. Tian, D.-H. Qu, Highly ordered supramolecular assembled networks tailored by bioinspired H-bonding confinement for recyclable ion-transport materials, CCS Chem. 5 (6) (2023) 1422–1432, https://doi.org/10.31635/ccschem.022.202202158.
[44] Q. Zhang, Y. Deng, C.-Y. Shi, B.L. Feringa, H. Tian, D.-H. Qu, Dual closed-loop chemical recycling of synthetic polymers by intrinsically reconfigurable poly (disulfides), Matter 4 (4) (2021) 1352–1364, https://doi.org/10.1016/j.matt.2021.01.014.
[45] B. Sieredzinska, Q. Zhang, K. J. van den Berg, J. Flapper, B.L. Feringa, Photo-crosslinking polymers by dynamic covalent disulfide bonds, Chem. Commun. 57 (77) (2021) 9838–9841, https://doi.org/10.1039/D1CC03648C.
[46] Y. Deng, Q. Zhang, D. Qu, H. Tian, B.L. Feringa, A chemically recyclable crosslinked polymer network enabled by orthogonal dynamic covalent chemistry, Angew. Chem. Int. Ed. 61 (39) (2022) e202209100, https://doi.org/10.1002/anie.202209100.
[47] B. Wang, Q. Zhang, Z. Wang, C. Shi, X. Gong, H. Tian, D. Qu, Acid-catalyzed disulfide-mediated reversible polymerization for recyclable dynamic covalent materials, Angew. Chem. Int. Ed. 62 (11) (2023), https://doi.org/10.1002/anie.202215329.
[48] T. Du, B. Shen, J. Dai, M. Zhang, X. Chen, P. Yu, Y. Liu, Controlled and regioselective ring-opening polymerization for poly(disulfide)s by anion-binding catalysis, J. Am. Chem. Soc. 145 (50) (2023) 27788–27799, https://doi.org/10.1021/jacs.3c10708.
[49] X. Zhang, R.M. Waymouth, 1,2-Dithiolane-Derived dynamic, covalent materials: cooperative self-assembly and reversible cross-linking, J. Am. Chem. Soc. 139 (10) (2017) 3822–3833, https://doi.org/10.1021/jacs.7b00039.
[50] G.A. Barcan, X. Zhang, R.M. Waymouth, Structurally dynamic hydrogels derived from 1,2-dithiolanes, J. Am. Chem. Soc. 137 (17) (2015) 5650–5653, https://doi.org/10.1021/jacs.5b02161.
[51] Y. Liu, Y. Jia, Q. Wu, J.S. Moore, Architecture-controlled ring-opening polymerization for dynamic covalent poly(disulfide)s, J. Am. Chem. Soc. 141 (43) (2019) 17075–17080, https://doi.org/10.1021/jacs.9b08957.
[52] NMR 3D Analysis Photopolymerization, Advances in Polymer Science, vol. 170, Springer Berlin Heidelberg, Berlin, Heidelberg, 2004, https://doi.org/10.1007/b12766.
[53] J.G. Kloosterboer, Network Formation by chain crosslinking photopolymerization and its applications in electronics, Electronic Applications; Advances in Polymer Science 84 (1988) 1–61, https://doi.org/10.1007/BFb0025902. Springer-Verlag: Berlin/Heidelberg.
[54] Y. Yagci, S. Jockusch, N.J. Turro, Photoinitiated polymerization: advances, challenges, and opportunities, Macromolecules 43 (15) (2010) 6245–6260, https://doi.org/10.1021/ma1007545.
[55] P.R. Brown, J.O. Edwards, Effect of solvent on the photolysis of alpha-lipoic acid, J. Org. Chem. 34 (10) (1969) 3131–3135, https://doi.org/10.1021/jo01262a072.
[56] J.A. Barltrop, P.M. Hayes, M. Calvin, The chemistry of 1, 2-dithiolane (trimethylene disulfide) as a model for the primary quantum conversion act in photosynthesis, J. Am. Chem. Soc. 76 (1954) 4348–4367, https://doi.org/10.1021/ja01646a029.
[57] D.F. Bradley, M. Calvin, The effect of thioctic acid on the quantum efficiency of the hill reaction in intermittent light, Proc. Natl. Acad. Sci. USA 41 (1955), https://doi.org/10.1073/pnas.41.8.563.
[58] B.R. Nelson, B.E. Kirkpatrick, C.E. Miksch, M.D. Davidson, N.P. Skillin, G.K. Hach, A. Khang, S.N. Hummel, B.D. Fairbanks, J.A. Burdick, C.N. Bowman, K.S. Anseth, Photoinduced dithiolane crosslinking for multiresponsive dynamic hydrogels, Adv. Mater. (2023) 2211209, https://doi.org/10.1002/adma.202211209.
[59] C. Shi, D. He, B. Wang, Q. Zhang, H. Tian, D. Qu, A dynamic supramolecular H-bonding network with orthogonally tunable clusteroluminescence, Angew. Chem. 135 (3) (2023) e202214422, https://doi.org/10.1002/ange.202214422.
[60] C. Nacci, M. Schied, D. Civita, E. Magnano, S. Nappini, I. Píš, L. Grill, Thermal- vs light-induced on-surface polymerization, J. Phys. Chem. C 125 (41) (2021) 22554–22561, https://doi.org/10.1021/acs.jpcc.1c06914.
[61] A. Kisanuki, Y. Kimpara, Y. Oikado, N. Kado, M. Matsumoto, K. Endo, Ring-opening polymerization of lipoic acid and characterization of the polymer,

J. Polym. Sci. Part Polym. Chem. 48 (22) (2010) 5247–5253, https://doi.org/10.1002/pola.24325.
[62] K. Endo, T. Shiroi, N. Murata, G. Kojima, T. Yamanaka, Synthesis and characterization of poly(1,2-dithiane), Macromolecules 37 (9) (2004) 3143–3150, https://doi.org/10.1021/ma021237d.
[63] L. Field, R.B. Barbee, Organic disulfides and related substances. XXVI. Preparation and oxidation of cyclic disulfides, J. Org. Chem. 34 (1) (1969) 36–41, https://doi.org/10.1021/jo00838a010.
[64] K. Endo, T. Yamanaka, Copolymerization of lipoic acid with 1,2-dithiane and characterization of the copolymer as an interlocked cyclic polymer, Macromolecules 39 (12) (2006) 4038–4043, https://doi.org/10.1021/ma060063n.
[65] W.J. Chung, J.J. Griebel, E.T. Kim, H. Yoon, A.G. Simmonds, H.J. Ji, P.T. Dirlam, R. S. Glass, J.J. Wie, N.A. Nguyen, B.W. Guralnick, J. Park, Á. Somogyi, P. Theato, M. E. Mackay, Y.-E. Sung, K. Char, J. Pyun, The use of elemental sulfur as an alternative feedstock for polymeric materials, Nat. Chem. 5 (6) (2013) 518–524, https://doi.org/10.1038/nchem.1624.
[66] D.P. Shannon, J.D. Moon, C.W. Barney, N.J. Sinha, K.-C. Yang, S.D. Jones, R. V. Garcia, M.E. Helgeson, R.A. Segalman, M.T. Valentine, C.J. Hawker, Modular synthesis and patterning of high-stiffness networks by postpolymerization functionalization with iron–catechol complexes, Macromolecules 56 (6) (2023) 2268–2276, https://doi.org/10.1021/acs.macromol.2c02561.
[67] C.J. Carrano, H. Drechsel, D. Kaiser, G. Jung, B. Matzanke, G. Winkelmann, N. Rochel, A.M. Albrecht-Gary, Coordination chemistry of the carboxylate type siderophore rhizoferrin: the iron(III) complex and its metal analogs, Inorg. Chem. 35 (22) (1996) 6429–6436, https://doi.org/10.1021/ic960526d.
[68] S. Zheng, H. Xue, J. Yao, Y. Chen, M.A. Brook, M.E. Noman, Z. Cao, Exploring lipoic acid-mediated dynamic bottlebrush elastomers as a new platform for the design of high-performance thermally conductive materials, ACS Appl. Mater. Interfaces 15 (34) (2023) 41043–41054, https://doi.org/10.1021/acsami.3c09826.
[69] T. Suzuki, Y. Nambu, T. Endo, Radical copolymerization of lipoamide with vinyl monomers, Macromolecules 23 (6) (1990) 1579–1582, https://doi.org/10.1021/ma00208a004.
[70] K. Ikemura, K. Kojima, T. Endo, Y. Kadoma, Effect of the combination of dithiooctanoate monomers and acidic adhesive monomers on adhesion to precious metals, precious metal alloys and non-precious metal alloys, Dent. Mater. J. 30 (4) (2011) 469–477, https://doi.org/10.4012/dmj.2010-151.
[71] K. Ikemura, K. Kojima, T. Endo, Y. Kadoma, Effect of novel dithiooctanoate monomers, in comparison with various sulfur-containing adhesive monomers, on adhesion to precious metals and alloys, Dent. Mater. J. 30 (1) (2011) 72–78, https://doi.org/10.4012/dmj.2010-119.
[72] C. Luo, Q. Dong, Z. Zheng, X. Ding, Y. Peng, Light-tunable thermosensitivity of polymer-coated gold nanoparticles achieved by light-controlled molecular recognition: light-tunable thermosensitivity of polymer-coated gold, Macromol. Chem. Phys. 212 (13) (2011) 1360–1365, https://doi.org/10.1002/macp.201100046.
[73] X. Chen, J. Lawrence, S. Parelkar, T. Emrick, Novel zwitterionic copolymers with dihydrolipoic acid: synthesis and preparation of nonfouling nanorods, Macromolecules 46 (1) (2013) 119–127, https://doi.org/10.1021/ma301288m.
[74] S. Impellizzeri, B. McCaughan, J.F. Callan, F.M. Raymo, Photoinduced enhancement in the luminescence of hydrophilic quantum dots coated with photocleavable ligands, J. Am. Chem. Soc. 134 (4) (2012) 2276–2283, https://doi.org/10.1021/ja209873g.
[75] H. Tang, N.V. Tsarevsky, Lipoates as building blocks of sulfur-containing branched macromolecules, Polym. Chem. 6 (39) (2015) 6936–6945, https://doi.org/10.1039/C5PY01005E.
[76] M. Raeisi, N.V. Tsarevsky, Radical ring-opening polymerization of lipoates: kinetic and thermodynamic aspects, J. Polym. Sci. 59 (8) (2021) 675–684, https://doi.org/10.1002/pol.20200765.
[77] B.-S. Wang, D.-H. Qu, The many ways for reversible polymerization of 1,2-dithiolanes, Chem. Lett. 52 (6) (2023) 496–502, https://doi.org/10.1246/cl.230142.
[78] G. Gasparini, E.-K. Bang, G. Molinard, D.V. Tulumello, S. Ward, S.O. Kelley, A. Roux, N. Sakai, S. Matile, Cellular uptake of substrate-initiated cell-penetrating poly(disulfide)s, J. Am. Chem. Soc. 136 (16) (2014) 6069–6074, https://doi.org/10.1021/ja501581b.
[79] E.-K. Bang, G. Gasparini, G. Molinard, A. Roux, N. Sakai, S. Matile, Substrate-initiated synthesis of cell-penetrating poly(disulfide)s, J. Am. Chem. Soc. 135 (6) (2013) 2088–2091, https://doi.org/10.1021/ja311961k.
[80] M. Uchiyama, Y. Murakami, K. Satoh, M. Kamigaito, Synthesis and degradation of vinyl polymers with evenly distributed thioacetal bonds in main chains: cationic DT copolymerization of vinyl ethers and cyclic thioacetals, Angew. Chem. 135 (4) (2023) e202215021, https://doi.org/10.1002/ange.202215021.
[81] G.M. Scheutz, J.L. Rowell, S.T. Ellison, J.B. Garrison, B.S. Sumerlin, Harnessing strained disulfides for photocurable adaptable hydrogels, Macromolecules 53 (10) (2020) 4038–4046, https://doi.org/10.1021/acs.macromol.0c00604.
[82] G.M. Scheutz, J.L. Rowell, F.-S. Wang, K.A. Abboud, C.-H. Peng, B.S. Sumerlin, Synthesis of functional 1,2-dithiolanes from 1,3-bis- *tert* -butyl thioethers, Org. Biomol. Chem. 18 (33) (2020) 6509–6513, https://doi.org/10.1039/D0OB01577F.
[83] A.J. Parker, N. Kharasch, The scission of the sulfur-sulfur bond, Chem. Rev. 59 (4) (1959) 583–628, https://doi.org/10.1021/cr50028a003.
[84] J. Houk, G.M. Whitesides, Structure-reactivity relations for thiol-disulfide interchange, J. Am. Chem. Soc. 109 (22) (1987) 6825–6836, https://doi.org/10.1021/ja00256a040.
[85] M.A. Alraddadi, V. Chiaradia, C.J. Stubbs, J.C. Worch, A.P. Dove, Renewable and recyclable covalent adaptable networks based on bio-derived lipoic acid, Polym. Chem. 12 (40) (2021) 5796–5802, https://doi.org/10.1039/D1PY00754H.
[86] R. Singh, G.M. Whitesides, Degenerate intermolecular thiolate-disulfide interchange involving cyclic five-membered disulfides is faster by ~10^23 than that involving six- or seven-membered disulfides, J. Am. Chem. Soc. 112 (17) (1990) 6304–6309, https://doi.org/10.1021/ja00173a018.