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Enhanced Degradation of Vinyl Copolymers Based on Lipoic Acid

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ABSTRACT

The introduction of degradable units into the backbone of commodity vinyl polymers represents a major opportunity to address the societal challenge of plastic waste and polymer recycling. Previously, we reported the facile copolymerization of α-lipoic acid derivatives containing 1,2-dithiolane rings with vinyl monomers leading to the incorporation of degradable S–S disulfide bonds along the backbone at relatively high dithiolane monomer feed ratios. To further enhance the recyclability of these systems, here we describe a facile and user-friendly strategy for backbone degradation at significantly lower dithiolane loading levels through cleavage of both S—S and S—C backbone units. Copolymers of *n*-butyl acrylate (*n*BA) or styrene (St) with small amounts of either α-lipoic acid (LA) or ethyl lipoate (ELp) dissolved in DMF were observed to undergo efficient degradation when heated at 100°C under air. For example, at only 5 mol% ELp, a high molecular weight poly(ELp-*co*-*n*BA) ($M_n = 62\,\mathrm{kg\,mol^{-1}}$) degraded to low molecular weight oligomers ($M_n = 3.2\,\mathrm{kg\,mol^{-1}}$) by simple heating in DMF. In contrast, extended heating of either poly(*n*BA) or poly(St) homopolymers under the same conditions did not lead to any change in molecular weight or cleavage of the C–C backbone. This novel approach allows for the effective degradation of vinyl-based polymers with negligible impact on properties and performance due to the low levels of dithiolane incorporation.

1 | Introduction

Commodity vinyl polymers, including polyacrylates and polystyrene, are produced globally on an enormous scale for a myriad of applications [1–3]. However, the life cycle of these materials is a concern, in part because of their limited degradability due to the chemical inertness of C—C bonds along vinyl polymer backbones. Consequently, the build-up of plastic waste in the environment remains a major societal issue [4, 5]. A simple and cost-efficient method to incorporate degradability into commodity vinyl polymers is therefore a grand challenge for polymer chemistry [6–9]. One common strategy is through copolymerization with cyclic monomers such as cyclic ketene acetals [10–14], macrocyclic allylic sulfides [15], or dibenzo[c,e]oxepane-5-thiones [16–18]. Incorporating these repeat units leads to the introduction of cleavable ester or thioester linkages into the C—C backbone. As a result, on-demand degradation of these backbone-functionalized vinyl copolymers is possible and has been demonstrated in the presence of chemical agents (i.e., base/acid) or with external stimuli (heat, ultraviolet light, etc.). However, the synthesis of these cyclic monomers is not straightforward, which impacts their broad applicability and commercial translation. A more user-friendly and cost-effective cyclic monomer for radical ring-opening copolymerization would be impactful and useful in the context of backbone-degradable vinyl materials.

Recently, we reported that a variety of acrylate monomers undergo both traditional [19, 20] and controlled [21] radical polymerization with α-lipoic acid (LA)—a commercially available and naturally occurring small molecule widely used as a nutritional supplement and gaining popularity as a tool in polymer synthesis [22–25]. From a copolymerization viewpoint, the key structural feature in α-lipoic acid and derivatives such as its ethyl ester (ethyl lipoate, ELp) is a strained 5-membered cyclic ring containing a disulfide bond ("dithiolane") that undergoes ring-opening polymerization under radical [19–22, 26], cationic [27], or anionic conditions [28, 29]. In radical copolymerization, ring opened dithiolane units are incorporated into the C—C backbone of vinyl copolymers with S—S bonds formed by dithiolane–dithiolane diad sequences [30–32]. Based on the reactivity and dynamic nature of these disulfide units, we previously demonstrated the efficient degradation of high molecular weight acrylate–lipoate copolymers under reductive conditions [19–21, 33]. However, to achieve appreciable degradability, high loadings of dithiolane monomer (~30%–40%) were required because many lipoate units are incorporated not as lipoate–lipoate diads but with lipoate–acrylate connectivity that forms less-reactive C—S thioethers. To minimize the loading of dithiolane monomer, a more efficient degradation strategy is needed that leverages chemistry which cleaves both S—S and C—S bonds.

To identify enhanced degradation conditions, a useful structural comparison can be made between lipoate–acrylate diads and the product that is obtained by the thiol–Michael addition of a thiol to an acrylate derivative. The latter has been shown to be a reversible reaction with the adducts being utilized as dynamic covalent bonds [34–36]. Konkolewicz et al. investigated the dynamics of these thiol–Michael reactions in the design of dynamic polymer networks which were demonstrated to have healable properties and unique mechanical performance [37]. Here, it was hypothesized that conditions promoting retro thiol–Michael reactions involving oxidation of sulfur to sulfoxides and sulfones would not only cleave S—S disulfide bonds but also the more numerous C—S thioether bonds. If true, degradation and cleavage of vinyl copolymer backbones should then occur at significantly lower levels of lipoate incorporation (Figure 1).

2 | Results and Discussion

To investigate conditions for the enhanced degradation of lipoate-based vinyl copolymers, a series of high molecular weight ethyl lipoate (ELp)/*n*-butyl acrylate (*n*BA) copolymers was initially selected as a model system. These materials are convenient because high molecular weights are readily achieved by conventional free-radical polymerization and copolymer composition is easily determined by ^{1}H NMR spectroscopy. For example, free-radical copolymerization of ELp (5 mol%) and *n*BA (95 mol%) was conducted at 70°C in toluene with AIBN as a thermal initiator (total monomer concentration = 2 M, monomer: initiator = 200:1). After 2 h, the copolymer was isolated by precipitation and shown to have a molecular weight ($M_n = 62$ kDa) in agreement with prior studies (Figure 2) [19]. Further analysis by ^{1}H NMR spectroscopy and comparison of the integration values for the unique methyl (CH_3) resonances of the ELp and *n*BA repeat units indicated the level of lipoate incorporation was ~6.1 mol%, which is in accord with the feed ratio of 5 mol%.

For this model copolymer system, a range of degradation conditions were investigated (Figure 2). We initially examined reductive cleavage of the backbone by treatment of a poly(ELp-*co*-*n*BA) ($M_w = 108$ kDa, $M_n = 62$ kDa) with tris(2-carboxyethyl)phosphine hydrochloride (TCEP), which selectively targets S—S disulfide bonds [19]. In agreement with our prior results, only a minimal reduction in molecular weight was observed at this low loading of ethyl lipoate (entry 1, $M_{n,\text{degraded}} = 54$ kDa) as the number of lipoate–lipoate diads formed under these polymerization conditions (2 M and 70°C) is small; we estimate there are only ~2–3 disulfides per chain based on the degree of polymerization and the statistical frequency of lipoate–lipoate diads.

With the model copolymer showing only a minor reduction in molecular weight upon treatment with TCEP, other degradation conditions potentially targeting C—S bonds along the backbone were studied. Treatment with a weak base, Na_2CO_3 in THF/H_2O, led to no change in molecular weight (entry 2) while treatment with a strong base (potassium *t*-butoxide, *t*-BuOK in THF, entry 3) resulted in decomposition of both the model poly(ELp-*co*-*n*BA) system as well as a control poly(*n*BA) homopolymer, presumably through partial hydrolysis of the ester side chains (see Supporting Information). Backbone cleavage was then examined under thermal conditions with initial heating in a non-polar solvent such as toluene (at 90°C) or chlorobenzene (at 100°C) leading to minimal change in molecular weight (entries 4 and 5). In direct contrast, thermolysis of the poly(ELp-*co*-*n*BA) in a polar solvent such as DMF or NMP at 100°C in the air for 18 h resulted in significant backbone cleavage with the molecular weight decreasing from 62 kg mol^{-1} to 3.2 and 2.2 kg mol^{-1} respectively (entry 6 and 7). Polar solvents are well known to accelerate the rate of reverse thio-Michael reactions, which may contribute to the reactivity observed in this system [38, 39]. The significant change in reactivity for a poly(ELp-*co*-*n*BA) (ELp composition = 6.1 mol%) is demonstrated in Figure 3 where the SEC trace for the starting copolymer showed little difference after treatment with TCEP while a major shift in elution time was observed after heating in DMF. This clear difference illustrates the influence of single lipoate units along the vinyl copolymer backbone and the benefit of cleaving both S—S and C—S units during the degradation process. Monitoring the evolution of molecular weight and dispersity over time for these DMF conditions was consistent with a controlled backbone cleavage process: SEC traces systematically shifted to lower molecular weights as the degradation progressed while maintaining a monomodal shape and consistent breadth (see Supporting Information).

To investigate the nature of this enhanced degradation process, a number of control experiments were performed. Addition of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-HO-TEMPO) as an anti-oxidant and radical trap to a DMF solution of the copolymer heated at 100°C for 18 h resulted in effective suppression of degradation with only a minor decrease in molecular weight being observed ($M_{n,\text{degraded}} = 38$ kDa, entry 8). Similarly, heating the copolymer in DMF under an inert atmosphere in the absence of oxygen led to no discernable change in molecular weight profile (see Supporting Information, Figure S26). Based on this result it is hypothesized that the degradation mechanism proceeds via an oxidative pathway, however, characterization of the products by NMR reveals no discernable differences for unlabeled materials. It is also known that dimethylamine can be generated by the decomposition of DMF at elevated temperatures [40, 41]. To understand the potential impact of basic conditions, the thermal degradation of poly(ELp-*co*-*n*BA) was conducted in toluene at 90°C with the addition of diisopropylamine. Again, a minimal reduction in molecular weight was observed ($M_{n,\text{degraded}} = 48$ kDa, entry 9). These two control experiments suggest that the enhanced degradation of lipoate-based copolymers in DMF at elevated temperatures may occur primarily by an oxidative mechanism and not a base-driven pathway. Moving forward, DMF was chosen as the prototypical degradation solvent due to its cost and availability over NMP.

The ability to degrade C—S bonds that are present along the backbone of vinyl polymers due to the incorporation of isolated lipoate repeat units allows for degradation to occur at much lower levels of lipoate incorporation. To investigate the effect of ELp incorporation, poly(ELp-*co*-*n*BA) copolymers with different ELp loadings were prepared in the same manner as

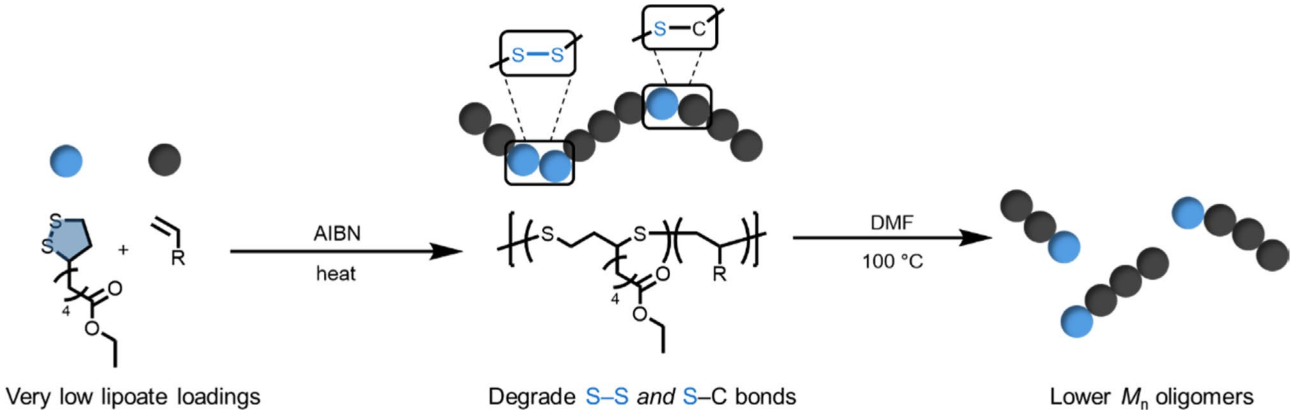
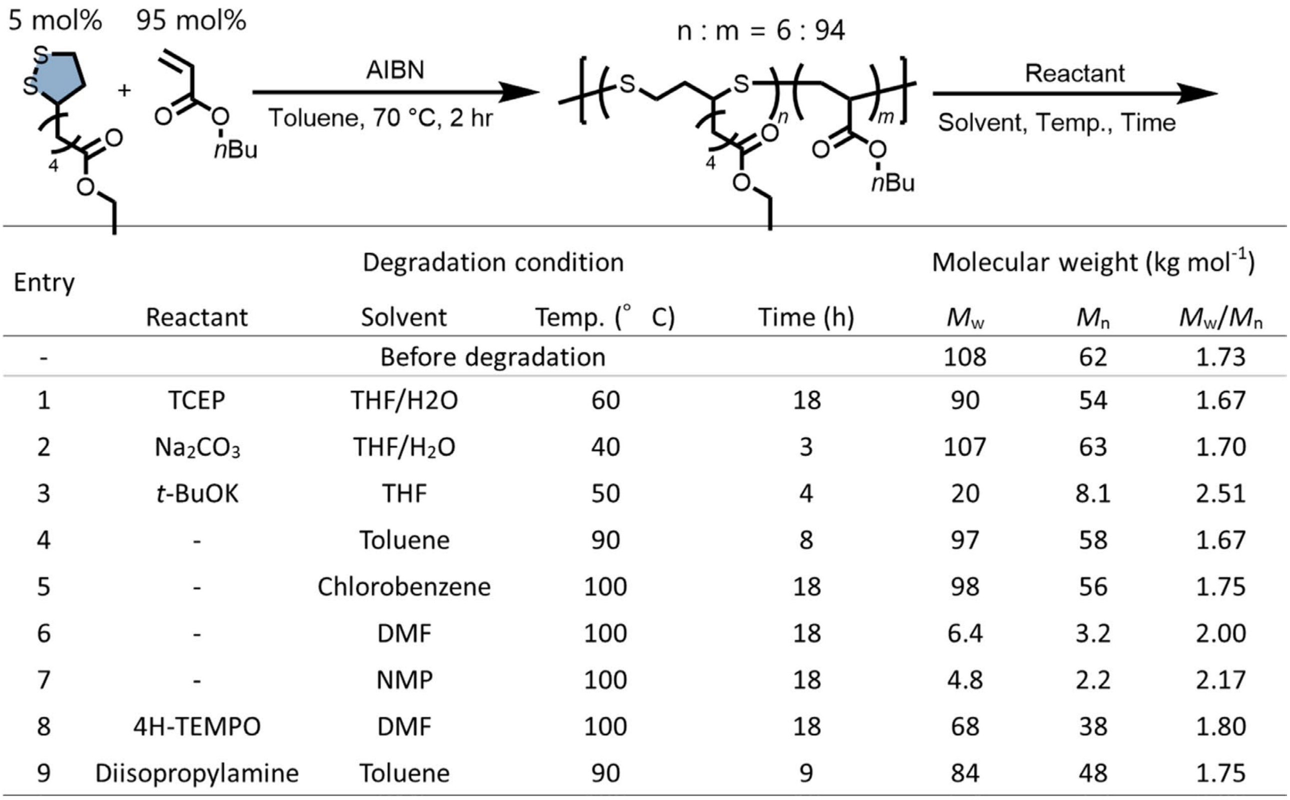


FIGURE 1 | In prior studies, a high mol% of lipoate incorporation was essential for degrading polymers due to exclusive cleavage of S—S disulfide bonds under reducing conditions. This work presents a novel approach using thermal and oxidative conditions that facilitate the cleavage of both S—S and C—S bonds. This advancement improves the efficiency of degradation into low-molar weight oligomers at significantly lower levels of lipoate incorporation.



Entry	Degradation condition				Molecular weight (kg mol^{-1})		
	Reactant	Solvent	Temp. (°C)	Time (h)	M_w	M_n	M_w/M_n
-		Before degradation			108	62	1.73
1	TCEP	THF/H2O	60	18	90	54	1.67
2	Na_2CO_3	THF/H_2O	40	3	107	63	1.70
3	*t*-BuOK	THF	50	4	20	8.1	2.51
4	-	Toluene	90	8	97	58	1.67
5	-	Chlorobenzene	100	18	98	56	1.75
6	-	DMF	100	18	6.4	3.2	2.00
7	-	NMP	100	18	4.8	2.2	2.17
8	4H-TEMPO	DMF	100	18	68	38	1.80
9	Diisopropylamine	Toluene	90	9	84	48	1.75

FIGURE 2 | Reaction scheme and impact of different degradation conditions on the molecular weight of ethyl lipoate/*n*-butyl acrylate copolymers. See the Supporting Information for detailed experimental procedures.

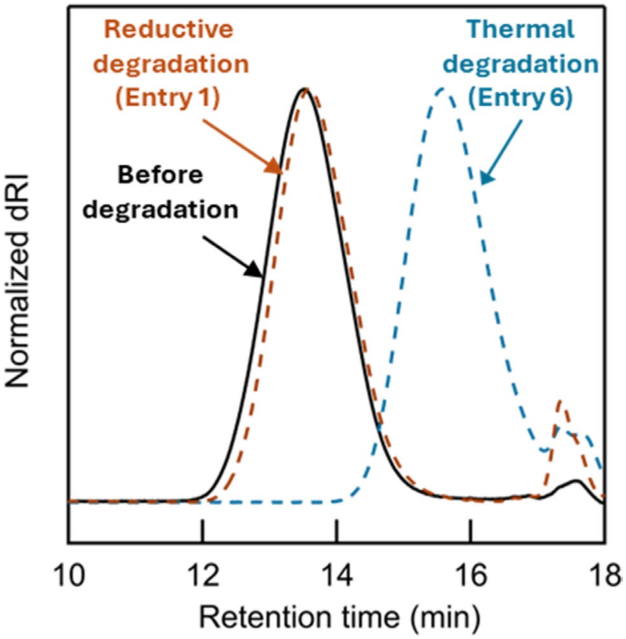


FIGURE 3 | Comparison of size exclusion chromatograms for poly(ELp-*co*-*n*BA) with 6.1 mol% ELp incorporation; parent copolymer (black solid line), after treatment with TCEP (orange dash), and after thermal degradation in DMF at 100°C for 18 h under air (blue dash).

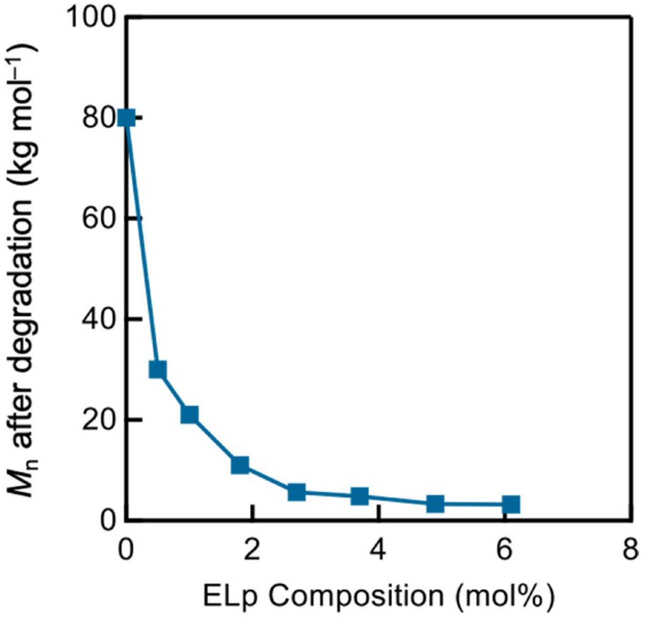


FIGURE 4 | Effect of ethyl lipoate content on the molecular weight after degradation following heating 1 M DMF solutions of different poly(ELp-*co*-*n*BA) copolymers at 100°C for 18 h under air.

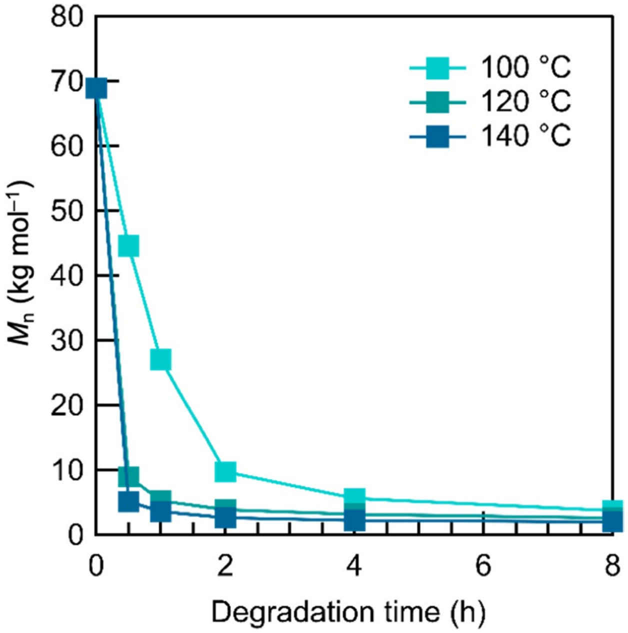
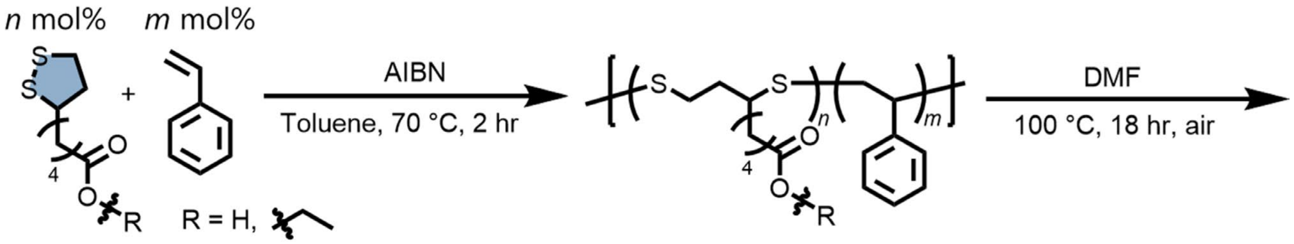


FIGURE 5 | Effect of degradation time and temperature on the molecular weight of degraded product after heating a 1 M DMF solution of the 6.1 mol% poly(ELp-*co*-*n*BA) copolymer under air.

described above by simply changing the ELp feed ratio. The resulting copolymers were shown to have similar molecular weights ($M_n = 62\sim80$ kg mol^{-1}) with ELp incorporations being characterized by ^{1}H NMR spectroscopy. A range of materials were synthesized containing lipoate loadings between 0.5 mol% ELp up to 6.1 mol%. Encouragingly, even at low levels of incorporation, heating at 100°C for 18 h in DMF results in a substantial reduction in molecular weight. At 1 mol% incorporation of ELp, the molecular weight of the copolymer was observed to decrease from 66 kg mol^{-1} to 21 kg mol^{-1}. Increasing the amount of lipoate further increased degradation until above 2 mol% ELp when all materials degraded to below 5 kg mol^{-1} (Figure 4). It should be noted that at these low levels of incorporation, minimal to no change in molecular weight was observed even after extended treatment with TCEP illustrating the low probability of lipoate–lipoate sequences and S–S bonds along the backbone of these copolymers.

The influence of temperature on the kinetics of degradation was then examined by heating the 6.1 mol% poly(ELp-*co*-*n*BA) copolymer at different temperatures and times under air. As can be seen in Figure 5, a rapid reduction in molecular weight was observed for all temperatures studied with a trend of decreasing degradation time with increasing temperature. For example, heating at 140°C for 1 h resulted in a significant decrease in molecular weight from 68 to 3.5 kg mol^{-1}. These results illustrate the efficiency and reproducibility of the thermal degradation process.

To demonstrate the versatility of lipoate derivatives as radical ring-opening building blocks for the synthesis of degradable vinyl copolymers, the copolymerization of styrene with either lipoic acid or ethyl lipoate followed by oxidative degradation in DMF was studied (Figure 6). Under similar conditions to the acrylate copolymerizations described above, copolymers of lipoic acid and styrene, poly(LA-*co*-St), and ethyl lipoate and styrene, poly(ELp-*co*-St), were prepared by traditional free-radical polymerization using AIBN as an initiator. As an illustrative example, copolymerization of a 4:96 mixture of lipoic acid and styrene afforded the desired poly(LA-*co*-St) copolymer ($M_n = 40$ kg mol^{-1}, $Đ = 1.9$) which was shown by ^{1}H NMR spectroscopy to have a lipoate incorporation level



Entry	Degradable Monomer	mol% lipoate (NMR)	M_n (kg mol^{-1}) Polymerized	M_n (kg mol^{-1}) Degraded
1	Lipoic Acid	0.4	36	15
2	Lipoic Acid	0.7	39	10
3	Lipoic Acid	1.7	36	9.1
4	Lipoic Acid	2.5	35	8.2
5	Lipoic Acid	3.7	40	8.1
6	Ethyl Lipoate	4.3	12	3.0

FIGURE 6 | Reaction scheme of lipoic acid or ethyl lipoate copolymers with styrene followed by degradation in DMF. Like with *n*-butyl acrylate, copolymerization and degradation were successful with increased degradable comonomer incorporation leading to a decrease in molecular weight after degradation.

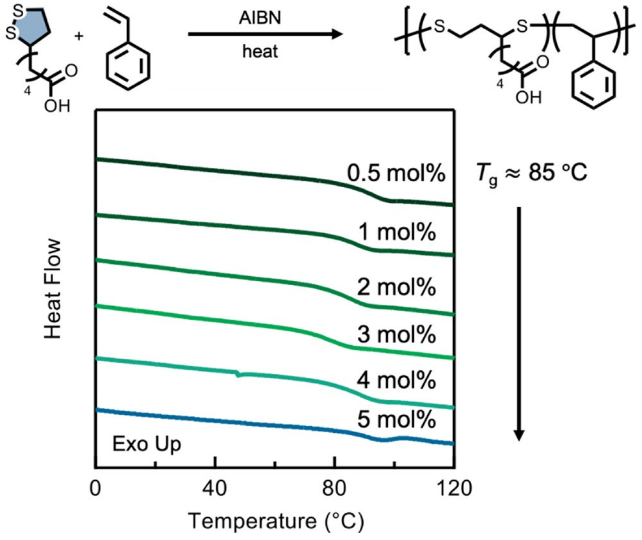


FIGURE 7 | Low loadings of lipoic acid have a minimal effect on the T_g of styrene copolymers but a tangible effect on degradability (recall, Figure 6).

of 3.7 mol% (see Supporting Information). Following purification, these copolymers were also subjected to a variety of different degradation conditions. As expected for polystyrene homopolymer, treatment with TCEP or DMF at elevated temperatures did not result in any change in molecular weight. Similarly, treatment of the 4.3 mol% poly(ELp-*co*-St) with TCEP led to little or no change in molecular weight, again due to the low probability of lipoate–lipoate diad sequences along the backbone at these molecular weights and loading levels. Significantly, heating the same copolymer at 100°C for 18 h in DMF under air resulted in a large change in molecular weight with size-exclusion chromatography showing a decrease from $M_n = 40$ to 8.1 kg mol^{-1}.

A key feature of this strategy for enhancing the backbone cleavage of vinyl copolymers based on lipoic acid is enabling a decrease in the level of comonomer incorporation, imparting degradability while retaining physical properties similar to the starting homopolymer. As shown above, loading levels (0.5–5 mol%) of lipoic acid or ethyl lipoate resulted in a significant reduction in molecular weight for the starting copolymer when heated in DMF at elevated temperatures under air. At these low levels of incorporation, the glass-transition temperature (T_g) for the copolymers ranges from 80°C to 85°C which is similar to that for poly(St) ($T_g \sim 90$°C) of comparable molecular weight (Figure 7). In contrast, a much higher loading of lipoic acid (> 10 mol%) is required for degradation strategies based on S—S cleavage only. Yet, copolymers containing 10 mol% lipoic acid—roughly the lower bound for successful disulfide bond cleavage—exhibit a T_g of 65°C ($M_n = 80$ kg mol^{-1}). Similarly, a T_g of 60°C ($M_n = 100$ kg mol^{-1}) was observed for a 20 mol% copolymer of ethyl lipoate and styrene. These results clearly illustrate the power of facile chemistry for cleaving both S—S and C—S bonds along the polymer backbone for the introduction of degradability while minimizing the impact on physical properties.

3 | Conclusions

Previous research has shown that high loadings of dithiolane repeat units (e.g., lipoic acid or ethyl lipoate) in vinyl-based copolymers enable degradation by reductive cleavage of S—S bonds formed within dithiolane–dithiolane diad units along the backbone. In this article, we present a more efficient strategy to achieve backbone degradation and significant reductions in molecular weight at much lower loading levels of dithiolane comonomer through the cleavage of both S—C and S—S bonds. These novel degradation conditions are particularly powerful because S—C bonds are created when single dithiolane repeat units are incorporated along the backbone, meaning they are more prevalent than lipoate–lipoate diads, especially at low loading levels. Through heating lipoic acid or ethyl lipoate copolymers with *n*BA and styrene (St) in DMF at elevated temperatures (100°C–140°C) under air, a dramatic reduction in molecular weight was observed with lipoate contents as low as 0.4 mol%. Crucially, at these low loadings, minimal changes in physical properties such as T_g were observed when compared with the corresponding homopolymers. This approach presents a practical solution to environmental concerns related to plastic waste by enhancing the degradability of otherwise long-lived and prevalent vinyl polymers. The accessibility of bio-renewable dithiolane derivatives, coupled with efficient polymer degradability at low loadings and a minimal impact on important physical properties may permit the drop-in use of these materials in industrial applications.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.