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Ring-opening copolymerization of hydroxyproline-derived thiolactones and lipoic acid derivatives†

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Ring-opening copolymerization is an important means to combine the properties of two or more monomers and fine-tune the properties of polymers. The copolymerization of two different types of monomers with full recyclability, however, has been rare. Here, we copolymerized the rigid 4-hydroxyproline-derived thiolactone with various lipoic acid derivatives that have flexible backbones to prepare poly(thioester-*co*-disulfide) copolymers with tunable thermal and mechanical properties. Owing to the full recyclability of both types of monomers, the resulting copolymers can be completely depolymerized to recycle both monomers in high monomer yields. This work provides a detailed understanding regarding the kinetics and controllability of the copolymerization system of thiolactone and 1,2-dithiolane, which may facilitate the design, modification, and strengthening of new recyclable polymer materials in the future.

Introduction

Dynamic polymers are materials containing a certain number of dynamic covalent bonds in the system.[1–3] Under the conditions of light, electricity, heat, pH, metal-ionic catalysis, *etc.*, dynamic polymers can realize rapid covalent bond exchange, so as to form bulk materials or gels with unique physical and chemical properties such as self-healing[4–10] and stimuli-responsiveness.[10–19] As the social and environmental crises caused by nondegradability of traditional polymers intensify, dynamic polymers have emerged as an important approach towards sustainability, material recovery and recycling, and functional intelligent materials.

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In the process of designing dynamic polymer systems, the selection of dynamic chemical bonds is of vital importance. To date, commonly used dynamic chemical bonds include ester,[20–24] thioester,[25–30] urea,[7,31–35] imine,[6,16] disulfide bonds,[4,10,30,36] *etc.* Among them, disulfide bonds are special in that they can realize dynamic exchange at relatively mild temperatures, or under light or base conditions. For this, polydisulfides (PDS) have been synthesized *via* various methods[37–41] and exploited for self-healing, adhesives, and other bio-based applications. In fact, PDS have been used for commercial purposes as aerospace sealants and chemical-resistant sealants since the last century. Many PDS are obtained from the ring-opening polymerization (ROP) of lipoic acid (Lp) and its derivatives (LpRs). Thanks to the dynamic thiol-disulfide exchange reactions occurring on the cell membrane, Matile[42–44] *et al.* applied PDS obtained by the ROP of LpRs for membrane penetration and drug delivery. Qu and Tian[45–49] *et al.* developed LpR-derived bulk materials, such as elastomers, hydrogels, adhesives, photo-responsive smart materials, *etc.* Despite these advances, however, the material properties of the LpR-derived PDS are usually soft and weak owing to the flexible main chain characteristics. For this reason, one often has to compromise the dynamic feature to compensate for the mechanical properties of PDS, or *vice versa*. To improve the mechanical strength of PDS materials, the most common strategy, for instance, applied in most bulk systems reported by Qu, Tian, and Feringa's teams mentioned above, is raising the crosslinking degree in the system, often to a level that is even higher than those of traditional rubber systems. Overall, there is a pressing need to improve the material properties of PDS, while maintaining their dynamic nature.

To tune the material properties of a polymer, one commonly used approach is to copolymerize two or more monomers that are distinctively different from each other. By inserting new side chains or even distinct backbones into the pristine polymers, dramatically different, and sometimes balanced, properties can be facilely achieved. Considering the

flexible backbone and weak disulfide bonds of LpR-derived PDS, we seek to introduce a more rigid and stable unit into the backbone of PDS systems through ring-opening copolymerization. The key, however, to this notion is to identify a different type of monomer that can on the one hand copolymerize with LpR and on the other hand provide the desired rigidity. Previously, our group has found that various N-substituted hydroxyproline-derived bicyclic lactones[50,51] and thiolactones (N^R-HPTL)[52] can be readily prepared and polymerized into high-molecular-weight polythioesters (PTE) containing a rigid pyrrolidine ring in the backbone. Given this complementary structural feature of N^R-HPTL with LpR, and the fact that the ROP of both monomers is based on thiolate anion-mediated chain propagation,[30] we reason that the copolymerization of the two types of monomers may be highly feasible and thus offer unprecedented poly(thioester-co-disulfide) (PTE-co-PDS) with unique and balanced properties. More importantly, since the ROP of both N^R-HPTL and LpR are kinetically and thermodynamically reversible near room temperature, we hypothesize that the resulting copolymers are intrinsically recyclable under mild conditions and regenerate monomers.[38,53,54] Of note, during the preparation of this manuscript, Professor Chen *et al.* reported a similar idea of copolymerizing thiolactones with LpR for the fabrication of recyclable vitrimers.[55]

Results and discussion

Random copolymerization of LpRs and N^Z-HPTL

According to previous studies on the homopolymerization of N^Z-HPTL and LpR monomers, dichloromethane (DCM) or CDCl$_3$ was used in the copolymerization for *in situ* nuclear magnetic resonance (NMR) characterization. Triethylamine (Et$_3$N) was used as the catalyst, and benzyl mercaptan (BnSH) or 1,2-dithioethane (EDT) was selected as the initiator. The reactions were conducted at −10 °C to obtain relatively high monomer conversions. Three LpRs with different side chains, namely aniline (LpNHPh), benzylamine (LpNHBn), and N-benzyl-6-hydroxyhexanamide (LpOCLNHBn), were synthesized (Fig. S1–S17†) for copolymerization with N^Z-HPTL to study the effect of the spacer length on the material properties (Fig. 1a). Taking LpNHBn as a model monomer, the ^{1}H NMR spectrum after quenching and precipitation into diethyl ether (Et$_2$O) reveals that the copolymerization with N^Z-HPTL gave a polymeric product displaying all sets of peaks originating from both monomers. Based on the integration of the characteristic peaks, the ratio of [N^Z-HPTL]/[LpNHBn] in the purified copolymer was calculated to be roughly 1/1.04, slightly lower than the feeding ratio of 1/1 (Fig. 1b). However, the kinetic study of the copolymerization process, determined by *in situ* ^{1}H NMR spectroscopy, repeatedly depicted a considerably faster consumption and higher incorporation rate of N^Z-HPTL than that of LpNHBn (Fig. 1c). We believed that the main reason for this "discrepancy" was due to precipitation loss, as LpNHBn and its polymeric units had lower solubility

in the precipitates. Size exclusion chromatography (SEC) analysis of copolymers **RP1–RP4** (entries 1–4, Table 1) showed unimodal peaks gradually shifting to the higher number-average molecular weight (M_n) region as the reaction proceeded, showing a clear pattern of chain growth (Fig. 1d). Elevating the initial total monomer-to-initiator ratio resulted in copolymers of almost linearly increasing M_n up to 75.8 kg mol^{-1} and moderate dispersity ($Đ$) in the range of 1.25–1.45 (Fig. 1e and entries 1–5, Table 1), indicating that the copolymerizations were fairly controlled. Differential scanning calorimetry (DSC) of a series of copolymers **RP5–RP7** (entries 5–7, Table 1) exhibited a monotonous increase of the glass transition temperature (T_g) as the feeding ratio, *i.e.* [N^Z-HPTL]$_0$/[LpNHBn]$_0$, was raised (Fig. 1f). Notably, the T_g values of all the copolymers were higher than that of the homopolymer of LpNHBn and lower than that of the homopolymer of N^Z-HPTL. The changes in the T_g value implied that these reactions indeed yielded copolymers rather than individual homopolymers. The results of more copolymerization reactions of N^Z-HPTL with various LpR monomers at different [N^Z-HPTL]$_0$/[LpR]$_0$/[I]$_0$ ratios are summarized in Table S1.† The T_g values of these copolymers were found to be highly tunable in the range of −47 to 58 °C, respectively, depending on the side chains of LpRs and copolymer compositions (Fig. 1g). Furthermore, bulk materials from **RP5–RP7** with different [N^Z-HPTL]$_0$/[LpNHBn]$_0$ ratios (entries 5–7, Table 1) were prepared, and splines were cut out for uniaxial tensile tests. Membranes and splines in entry 5 and entry 6 are self-supporting and have a similar yield strain at ~10%. **RP5** with a feeding ratio of [N^Z-HPTL]$_0$/[LpNHBn]$_0$ = 240/240 was the hardest one, with a yield point of ~1.58 MPa, and the elongation at break of no more than 2 times the original length. **RP6** with a feeding ratio of [N^Z-HPTL]$_0$/[LpNHBn]$_0$ = 180/240 has a relatively balanced strength and toughness, with a yield point of 0.46 MPa, and the elongation at break of over 6.79 times the original length. However, **RP7** with a feeding ratio of [N^Z-HPTL]$_0$/[LpNHBn]$_0$ = 120/240 was soft and sticky, and not self-supporting. It was stretchable to tens of times its original length but with a stress of only ~10 kPa (Fig. 1h and entries 5–7, Table 1). Overall, the results were consistent with our basic design of combining the rigid N^Z-HPTL and soft LpRs to modulate the material properties. The mechanical properties of the materials from these linear copolymers can be tuned in a fairly broad range, from hard and brittle, to soft and weak.

Depolymerization of the linear random copolymers

Considering that the homopolymers of both N^Z-HPTL and LpR are chemically recyclable under relatively similar and mild conditions, we sought to test the depolymerization of the copolymers. On treating the diluted copolymer solution (entry 2, Table 1) in acetonitrile with DTT and DBU at 65 °C, the solution gradually turned light yellow, suggesting the regeneration of the monomer LpNHBn. After quenching the reaction 0.5 hour later, evaporating all the solvent, and redissolving the residue in CDCl$_3$, all
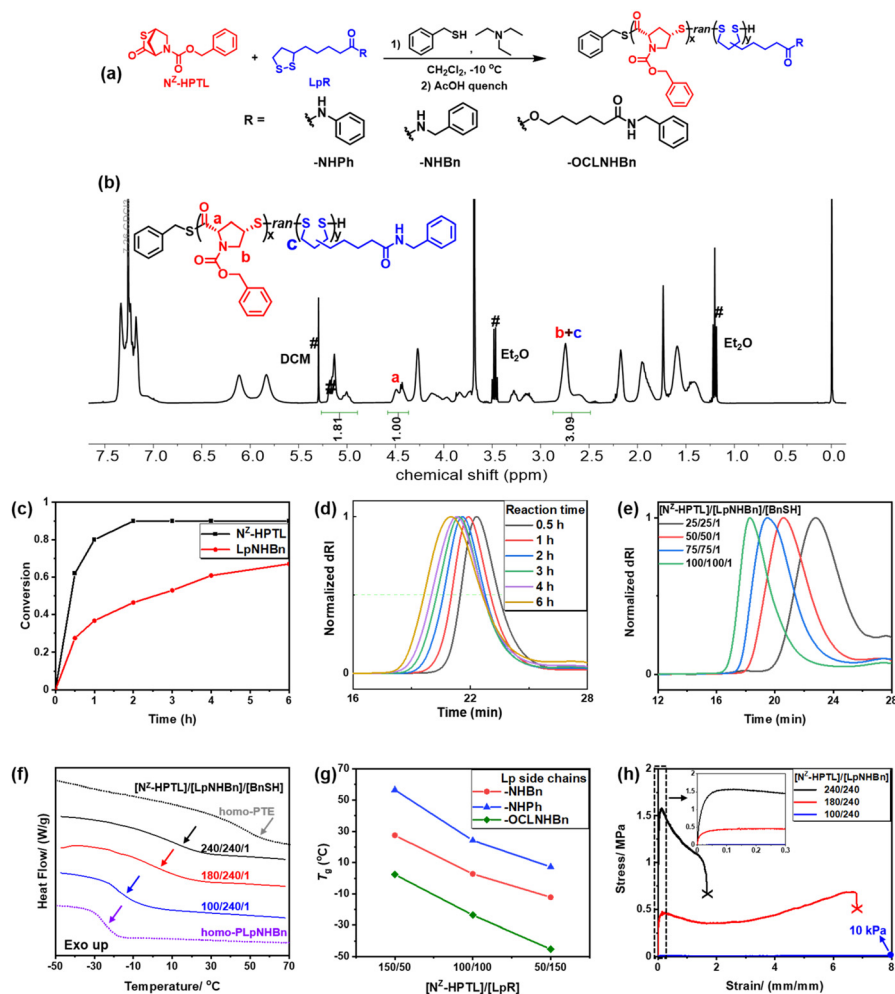
Fig. 1 Random copolymerization of N^Z-HPTL with various LpRs. (a) Structures of monomers and the scheme of the random copolymerization. (b) The structure and corresponding ^1H NMR spectrum of a copolymer **RP2**. (c) Plots of monomer conversion as a function of the reaction time (**RP4**). (d) Overlay of the SEC traces of **RP4** at different reaction time points. $[N^Z\text{-HPTL}]_0/[LpNHBn]_0/[BnSH]_0/[Et_3N]_0 = 100/100/1/3$. (e) Overlay of the SEC traces of copolymers of N^Z-HPTL and LpNHBn at different monomer-to-initiator ratios (**RP1–RP4**). (f) DSC traces of the homopolymer of N^Z-HPTL, the homopolymer of LpNHBn, and **RP5–RP7**. The second heating cycle was shown and the temperature was increased at a rate of 10 °C min^{-1}. (g) Plots of T_g of various copolymers as a function of the $[N^Z\text{-HPTL}]/[LpR]$ ratio. (h) Overlay of stress–strain curves of bulk materials from random copolymers **RP5–RP7** with varying N^Z-HPTL and LpNHBn ratios.

Table 1 Random copolymerization results of N^Z-HPTL and LpNHBn[a]

Entry	Name	$[N^Z\text{-HPTL}]_0/[LpNHBn]_0/[I]_0$	Time/h	$M_{n, SEC}$[b] (kg mol^{-1})	$Đ$[c]	N^Z-HPTL Conv.[d]/%	LpNHBn Conv.[d]/%	T_g/°C
1	**RP1**	25/25/1	2	9.86	1.23	>90	72	—
2	**RP2**	50/50/1	6	20.0	1.25	90	67	2.5
3	**RP3**	75/75/1	18	33.5	1.36	>90	71	—
4	**RP4**	100/100/1	24	60.8	1.37	>90	70	7.2
5	**RP5**	240/240/1	48	75.8	1.41	>90	65	8.2
6	**RP6**	180/240/1	48	69.6	1.39	88	67	−4.4
7	**RP7**	100/240/1	48	62.2	1.45	89	72	−24.4

[a] All polymerizations were initiated with BnSH in DCM in a refrigerator at −10 °C, $[M]_0 = [N^Z\text{-HPTL}]_0 + [LpNHBn]_0 = 2$ mol L^{-1}, 2 equiv. Et$_3$N (vs. BnSH) was used to catalyze the polymerization. [b] Determined by SEC in the THF mobile phase calibrated with the polystyrene standard. [c] Dispersity, determined by SEC. [d] Monomer conversions calculated from the integrations of the characteristic peaks in ^1H NMR spectra.

polymer peaks disappeared in the ^1H NMR spectrum (Fig. 2). The depolymerized products gave exclusively the peaks of the two monomers N^Z-HPTL and LpNHBn (and a small amount of the solvent), affording a higher than 90% yield of monomer recycling based on ^1H NMR spectra (Fig. 2).
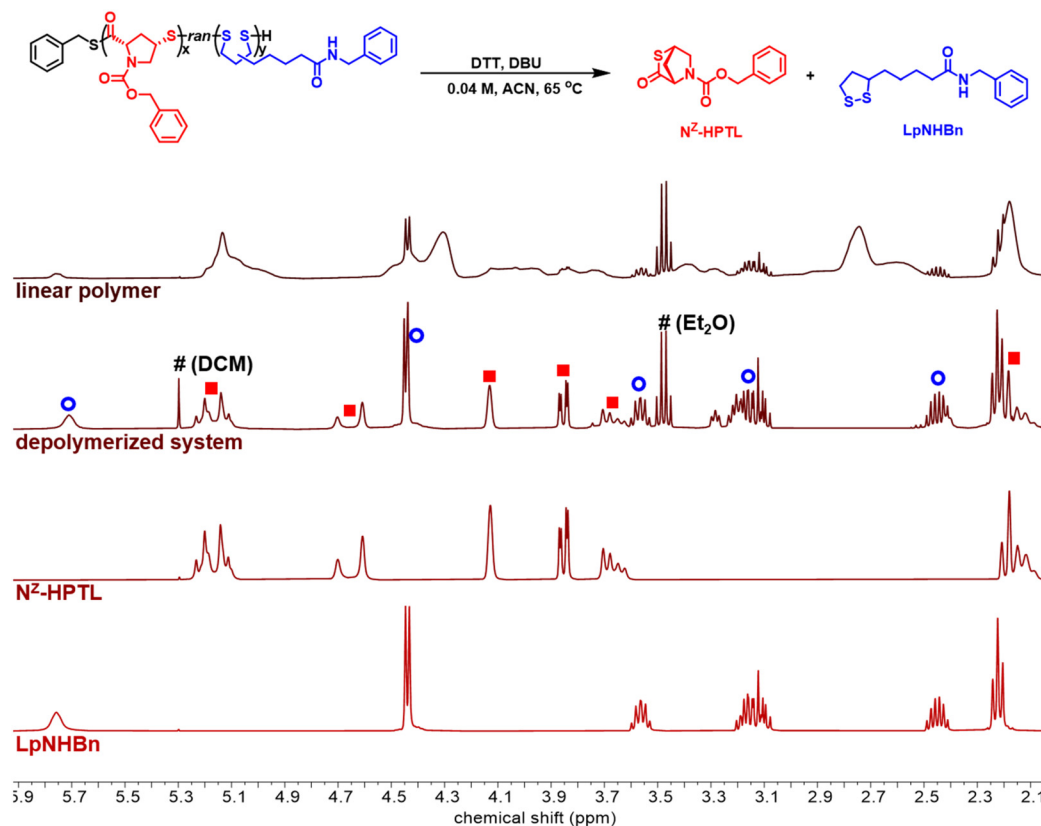
Fig. 2 Overlay of ^{1}H NMR spectra of the original linear polymer, the depolymerized system, and LpNHBn and N^Z-HPTL monomers as a comparison.

Quasi-block copolymerization of LpNHBn and N^Z-HPTL

In addition to the random copolymerization with premixed monomers, we also studied the quasi-block copolymerization by adding N^Z-HPTL *in situ* after the ROP of LpNHBn reached equilibrium (Table 2). Of note, by defining it as quasi-block, we refer to the situation that a small amount of remaining LpNHBn, given its high equilibrium monomer concentration, may insert into the block of N^Z-HPTL (Fig. 3a). Briefly, by using 1,2-dithioethane as a bifunctional initiator and Et$_3$N as the catalyst, the ROP of LpNHBn was allowed to reach equilibrium in 24 h with a conversion of ~65%. Upon the addition of N^Z-HPTL, ^{1}H NMR spectra indicated that ~90% of the thiolactone monomer was rapidly polymerized within 1 h, along with an additional ~10% conversion of the first monomer LpNHBn (Fig. 3b). In this way, a series of ABA type quasi-block

copolymers were successfully produced (Table 2 and Fig. S18–S23†). DSC characterization of these quasi-block copolymers in different [N^Z-HPTL]$_0$/[LpNHBn]$_0$ ratios (**BP1**–**BP3**) exhibited a clear T_g value close to that of the homopolymer of LpNHBn (Fig. 3c), which was strikingly different from the T_g values of the random copolymers shown in Fig. 1e and f. The second T_g value corresponding to the homo-PTE segment, however, was barely seen for the quasi-block copolymers. This was perhaps a result of the random insertion of LpNHBn into the PTE segments, which impaired the original microstructure of PTE (Fig. 3c and S24–S28†). Taken together, the above results convincingly demonstrated the acquisition of quasi-block copolymers of PTE and PDS. The mechanical properties of these quasi-block copolymers were also tested by uniaxial tensile tests, whose results were similar to those of the random copolymers. Splines of **BP1** and **BP2**, the two with [N^Z-HPTL]$_0$/

Table 2 Summary of the mechanical results of linear polymers from uniaxial tensile tests

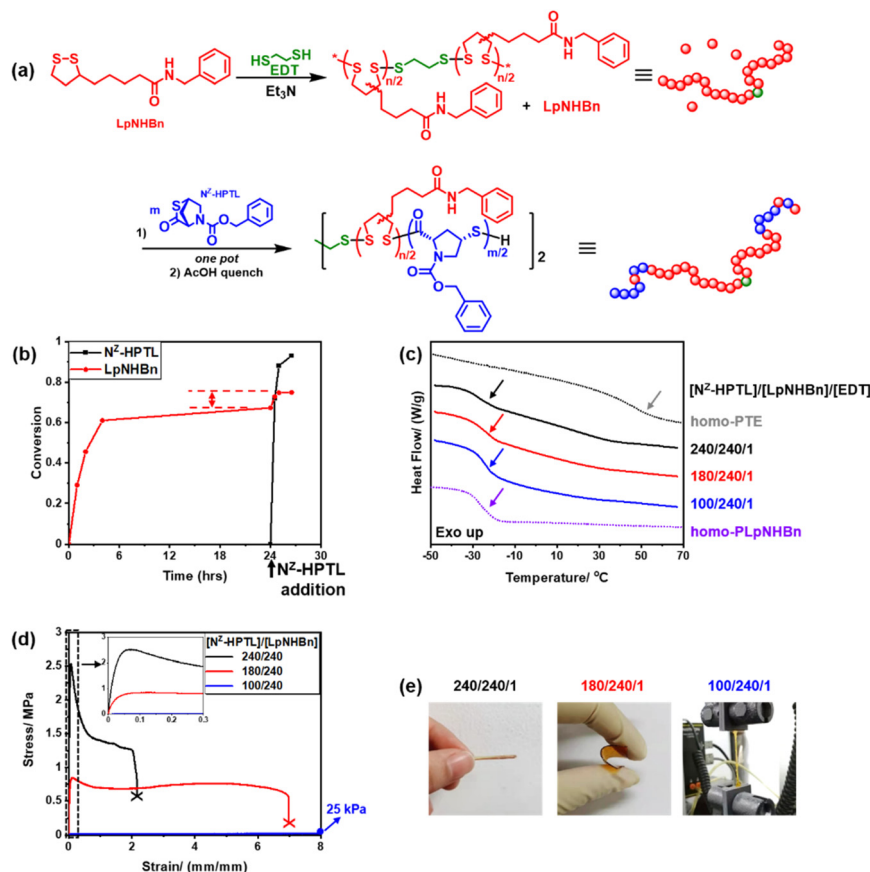| Entry	Name	[N^Z-HPTL]$_0$/[LpNHBn]$_0$/[I]$_0$	Feeding sequence	Yield point/MPa	Yield strain/%	Young's modulus/MPa	Elongation at break (mm mm^{-1})
1	**RP5**	240/240/1	Random	1.58	10.0	56.7	1.60
2	**RP6**	180/240/1	Random	0.46	10.9	16.7	6.79
3	**RP7**	100/240/1	Random	0.008	16.4	0.25	—
4	**BP1**	240/240/1	Quasi-block	2.53	6.9	87.1	2.05
5	**BP2**	180/240/1	Quasi-block	0.84	8.3	27.4	6.98
6	**BP3**	100/240/1	Quasi-block	0.015	31.1	0.40	—

Fig. 3 Quasi-block copolymerization of LpNHBn and N^Z-HPTL. (a) Scheme of the synthesis. (b) Plots of the monomer conversion as a function of the reaction time for the synthesis of the copolymer with a feeding ratio of [LpNHBn]/[EDT]/[Et₃N]/[N^Z-HPTL] = 100/1/5/100. (c) DSC traces of homo- and quasi-block copolymers (**BP1–BP3**) during the second heating cycle at a rate of 10 °C min⁻¹. (d) Overlay of stress–strain curves of bulk materials from quasi-block copolymers with varying N^Z-HPTL and LpNHBn ratios (**BP1–BP3**). (e) Photographs of bulk materials from quasi-block copolymers with varying N^Z-HPTL and LpNHBn ratios (**BP1–BP3**).

[LpNHBn]₀ ratios of 240/240 and 180/240, respectively, were self-supporting with similar yield strains at ~7%. The yield points of **BP1** and **BP2** were ~2.53 MPa and ~0.84 MPa, respectively, while **BP3** was soft and weak, with a stress of ~ 25 kPa even after stretching tens of times (Fig. 3d, e and entries 4–6, Table 2). Overall, the mechanical properties of the quasi-block copolymers were very close to those of the random copolymers with the same monomer ratios. Besides, quasi-block copolymers with the reversed feeding sequence, that is, N^Z-HPTL first and then LpNHBn, forming a "soft–hard–soft" structure, were also prepared for comparison (Table S2,† entries 4 and 5). The results of the following tensile tests indicate that the reversed quasi-block copolymers have a lower LpNHBn conversion, and therefore more brittle properties and much lower elongation at break (Fig. S29†).

of polymers from different feeding ratios, we demonstrated the basic copolymerization features of the two types of monomers. Bulk materials were prepared from the copolymers, and it was confirmed that the hydroxyproline polythioester with a typical pyrrolidine ring backbone structure has considerable rigidity, which is shown in the macroscopic view to improve the physical and mechanical properties of the poly lipoic acid derivatives, such as the glass transition temperature, tensile behavior of bulk materials, *etc*. In addition, chemical and mechanical recycling of copolymers is realized under mild conditions. This work provides a detailed understanding regarding the kinetics and controllability of the copolymerization system of thiolactone and 1,2-dithiolane, which may facilitate the design, modification, and strengthening of new recyclable polymer materials in the future.

Conclusions

To summarize, this paper reported the copolymerization of hydroxyproline-derived thiolactone and lipoic acid derivatives. Through kinetic characterization studies and thermal analysis

Author contributions

Yi Zhang: methodology, data curation, investigation, writing – original draft, and visualization. Hua Lu: supervision, concep-

tualization, project administration, funding acquisition, and writing – reviewing and editing.

Conflicts of interest

There are no conflicts to declare.

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