# Structure-Property Relationship Analysis of D-Penicillamine-Derived β-Polythioesters with Varied Alkyl Side Groups

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Ⓔ Electronic Supplementary Information

**Abstract**   The ring-opening polymerization of heterocyclic monomers and the reversed ring-closing depolymerization of corresponding polymers with neutral thermodynamics are broadly explored to establish a circular economy of next-generation plastics. Polythioesters (PTEs), analogues of polyesters, are emerging materials for this purpose due to their high refractive index, high crystallinity, dynamic property and responsiveness. In this work, we synthesize and polymerize a series of D-penicillamine-derived β-thiolactones (N$^R$PenTL) with varied side chain alkyl groups, and study the structure-property relationship of the resulting polymers. The obtained PTEs exhibit tunable glass transition temperature in a wide range of 130–50 °C, and melting temperature of 90–105 °C. In addition, copolymerizations of monomers with different side chains are effective in modulating material properties. The obtained homo and copolymers can be fully depolymerized to recycle monomers. This work provides a robust molecular platform and detailed structure-property relationship of PTEs with potential of achieving sustainable plastics.

**Keywords**   β-Polythioesters; Geminal dimethyl; Structure-property relationship; Chemical recycling to monomers

## INTRODUCTION

Polymer materials are extensively utilized in packaging, textiles, healthcare, and other areas of daily life due to their benefits of low cost, easy processing, and excellent performance.[1] Compared to 1950, the annual production of plastics had increased nearly 230-fold, reaching 459 million tons in 2019. However, traditional plastics are difficult to degrade and their end-of-life disposal poses significant social and environmental crisis, threatening the health of wildlife and human being.[2] Currently, there are merely less than 20% plastics physically or down-graded recycled, necessitating researches on new strategies that can allow sustainable production and complete recycling of novel degradable polymers.[3–9]

Among all strategies that are being developed, chemical recycling to monomers is believed to have the potential overcoming the traditional linear "monomer-polymer-waste" economic model of plastics and to create a closed-loop new model of "monomer-polymer-material-monomer".[8–11] Specifically, if monomers can be recovered under mild condi-

tions with low energy consumption and the resulting monomers can be repolymerized, then not only can recover the intrinsic materials and energy value of the plastics, avoid the property loss of traditional physical recycling in the meantime, but also reduce the overall environmental pollution. Ideally, a system that can successfully recover monomers should be thermodynamically neutral, *i.e.*, near zero kcal/mol in the Gibbs free energy change under standard conditions, thereby enabling selective polymerization or the reversed depolymerization under appropriate and mild conditions.[9–12]

Theoretically, all polymers obtained by ring-opening polymerization (ROP) have the potential to depolymerize back to cyclic monomers.[13] In recent years, ROP of heterocyclic compounds have been widely studied, producing degradable/recyclable polymers including polyesters,[14–20] polythioesters,[21–28] polycarbonates,[29–34] polyamides,[35,36] and polyacetals.[37,38] Among them, polyester materials are widely recognized for their excellent performance and renewable biomass feedstock. Polythioesters (PTEs), on the other hand, are a class of polymers in which the oxygen atoms in the polyester backbone are replaced with sulfur atoms.[24,26,39] The C—S bond (182 pm) is longer than the C—O bond (143 pm), while the bond angle of C—S—C (99.45°–99.5°) is significantly smaller than that of C—O—C (111.5°–112.8°).[40] In addition, the lone pair electrons of the sulfur atoms in thioesters are less capable of delocalization to the carbonyl group than

those of oxygen in the esters. All these differences can potentially affect the ring strain of the cyclic (thio)ester monomers, which determines the monomer's stability and polymerizability. In addition, compared to polyester analogues, PTEs usually exhibit enhanced crystallinity due to its larger dipole moments, stronger intermolecular interactions, and more rigid chain conformations.[25,40] Moreover, because of the reactivity and susceptibility to nucleophiles[41] and hydrolysis, thioesters are kinetically favored to undergo both polymerization and depolymerization, which is a great advantage for constructing dynamic covalent networks and responsive biomaterials.[42–46] Finally, the abundant sulfur elements in PTEs can sometimes lead to high refractive index, expanding the applications as high-value optical materials.[47]

Historically, PTEs have been prepared through anionic ROP of thiolactones (TLs) and thionolactones (TNLs) by Overberger, Weise[48,49] and Endo[50] since 1960s. The renaissance of PTE occurred in the past decade, with representative studies from Kiesewetter,[51] Suzuki,[52] Bowman,[53] Gutekunst,[54] Ren and Lu[55] since 2015. Notably, through judicious molecular design, a few works not only achieved controlled ROP of TLs/TNLs, but also the full recovery of pristine monomers from the obtained PTEs. For example, Lu et al. developed side-chain functionalized bridged bicyclic TLs and β-geminal dimethyl substituted β-TLs from amino acid feedstock.[21,22] Independently, Chen et al. and Tao et al. prepared bridged bicyclic TL,[23] and dithiolactones,[24,28] monothiodilactones,[26] respectively. Hong et al. synthesized biomass-derived γ-TNL for the controlled production of PTEs that can be recycled into γ-TL.[25,56] Zhu et al. prepared a class of 1,4-dithian-2-one with thioester and thioether functionalities.[27] All of the above studies have successfully prepared PTE materials with modest-to-good mechanical performance and brilliant recyclability.

In previous work, our group successfully developed a series of N-substituted β-geminal dimethyl β-TL monomers (N[R]-PenTL, Fig. 1) from natural species D-penicillamine in a modular, highly efficient, one-pot manner.[22] Thanks to the steric hindrance and conformational entropy effect of the geminal dimethyl group,[57,58] the controllability of both the forward chain propagation and backward depolymerization were effectively improved, producing a class of PTEs (termed as P(N[R]PenTE)) with circular material economy. However, the material properties of P(N[R]PenTE) are still suboptimal and a fundamental understanding of the structure-property relationship (SPR) of the system is still missing. Herein, we seek to conduct both homo and copolymerizations of N[R]PenTL, and carefully investigate the SPR by systematically varying the side chain R group of P(N[R]PenTE) (Fig. 1). The results of the study can potentially provide molecular insight of the system and lay a firm foundation for the design and synthesis of high-performance PTE materials.

## EXPERIMENTAL

Experimental details, ^{1}H- and ^{13}C-NMR spectra, high-resolution mass spectrometry, ATR-FTIR, DSC and DMA curves are presented detailly in the electronic supplementary information (ESI).

## RESULTS AND DISCUSSION

By adapting the previously reported method,[22] we synthesized a series of N[R]PenTL (R represents the carbon number and linear/branched structure of side chain alkyl group, e.g., C4 = n-butyl and iC4 = isobutyl). The monomers are colorless oils when the R groups are C6–C10, while other monomers are white solids (^{1}H- and ^{13}C-NMR, high-resolution mass spectra, in Figs. S1–S33 in ESI). Similar to previous ROP conditions,[21,22] these monomers were initiated by benzyl mercaptan (BnSH) and catalyzed by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or phosphazene ([t]BuP4) in bulk (or with as little as possible tetrahydrofuran (THF) to dissolve solid monomer) at room temperature. After reaching equilibrium of polymerization, the polymer chain ends were capped with iodoacetamide (IAA). White or light-yellow polymers were obtained with estimated yields of 25%–65% after precipitation and vacuum drying (Table 1, ^{1}H-NMR in Figs. S34–S44 in ESI). Among them, all the PTEs were soluble in common organic solvents (e.g., THF, N,N-dimethylformamide (DMF), chloroform, methanol, etc,) except
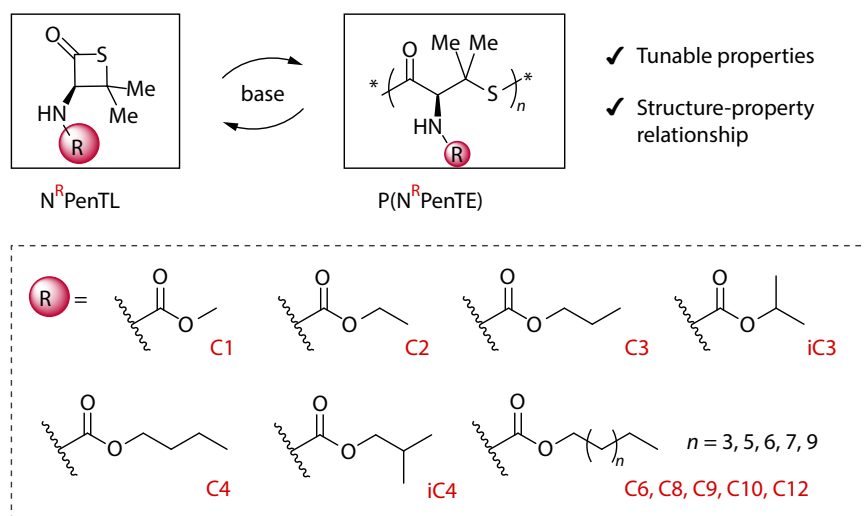


**Fig. 1** Synthetic scheme of the ROP of various N[R]PenTL and depolymerization of P(N[R]PenTE).

**Table 1**　Ring-opening polymerization results of N$^R$PenTL.

| Entry | R | Base | [M]$_0$/[I]$_0$/[base]$_0$ | Time (h) | $M_n^{cal\ a}$ (kg·mol$^{-1}$) | $M_n^{obt\ b}$ (kg·mol$^{-1}$) | Đ | Conv. [d] |
|---|---|---|---|---|---|---|---|---|
| 1 | C1 | DBU | 100:1:1 | 2 | 18.9 | – | – | – |
| 2 | C2 | DBU | 100:1:1 | 2 | 20.3 | – | – | – |
| 3 | C3 [e] | DBU | 100:1:1 | 2 | 21.7 | 13.4 | 1.19 | 71% |
| 4 | iC3 [f] | DBU | 100:1:1 | 2 | 21.7 | 13.1 | 1.08 | 40% |
| 5 | C4 [g] | DBU | 100:1:1 | 2 | 23.1 | 15.9 | 1.10 | 75% |
| 6 | iC4 [h] | DBU | 100:1:1 | 2 | 23.1 | 14.5 | 1.12 | 71% |
| 7 | C6 [i] | DBU | 100:1:1 | 2 | 25.9 | 20.8 | 1.22 | 78% |
| 8 | C8 [j] | DBU | 100:1:1 | 2 | 28.7 | 22.0 | 1.16 | 80% |
| 9 | C9 [k] | DBU | 100:1:1 | 2 | 30.1 | 24.8 | 1.08 | 76% |
| 10 | C10 [l] | DBU | 100:1:1 | 2 | 31.5 | 28.5 | 1.05 | 77% |
| 11 | C12 | DBU | 100:1:1 | 2 | 34.3 | 12.1 | 1.15 | 49% |
| 12 | C1 | $^tBuP_4$ | 300:1:1 | 12 | 56.7 | – | – | – |
| 13 | C2 | $^tBuP_4$ | 300:1:1 | 12 | 60.9 | – | – | – |
| 14 | C3 | $^tBuP_4$ | 300:1:1 | 12 | 65.1 | 42.1 | 1.21 | 66% |
| 15 | iC3 | $^tBuP_4$ | 300:1:1 | 12 | 65.1 | – | – | 17% |
| 16 | C4 | $^tBuP_4$ | 300:1:1 | 12 | 69.3 | 42.3 | 1.14 | 62% |
| 17 | iC4 | $^tBuP_4$ | 300:1:1 | 12 | 69.3 | 45.1 | 1.20 | 64% |
| 18 | C6 | $^tBuP_4$ | 300:1:1 | 12 | 77.7 | 66.8 | 1.19 | 63% |
| 19 | C8 | $^tBuP_4$ | 300:1:1 | 12 | 86.2 | 76.5 | 1.22 | 76% |
| 20 | C9 | $^tBuP_4$ | 300:1:1 | 12 | 90.4 | 80.9 | 1.29 | 74% |
| 21 | C10 | $^tBuP_4$ | 300:1:1 | 12 | 94.6 | 83.1 | 1.20 | 75% |
| 22 | C12 | $^tBuP_4$ | 300:1:1 | 12 | 102.9 | – | – | 12% |

[a] Calculated number-average molecular weight based on the feeding M/I ratio; [b] Obtained number-average molecular weight and [c] dispersity determined by SEC in DMF with 0.1 mol/L LiBr except entry 11 (in THF); [d] Monomer conversion, determined by $^1$H-NMR; The d$n$/d$c$ values of the corresponding polymers: [e] 0.0759, [f] 0.0869, [g] 0.0752, [h] 0.0772, [l] 0.0707, [j] 0.0780, [k] 0.0581 and [l] 0.0706.
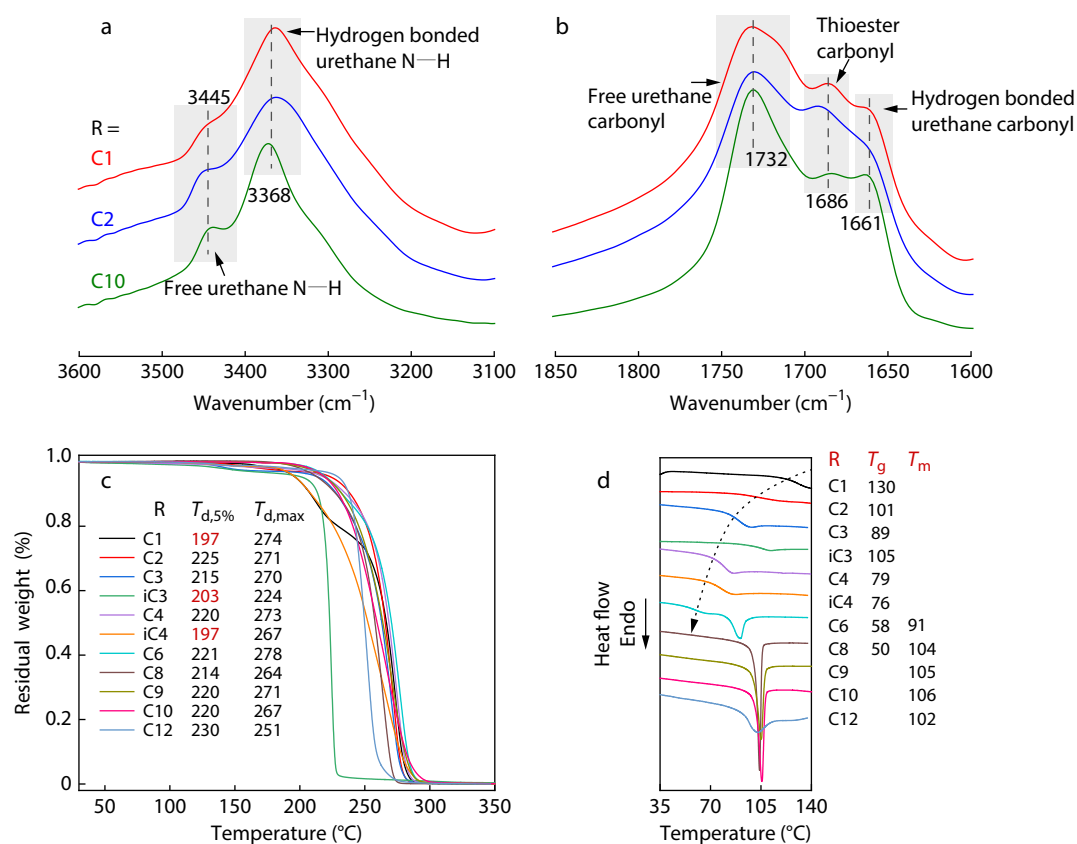


**Fig. 2**　(a) N−H and (b) carbonyl stretching region in IR spectra of P(N$^R$PenTE) (entries 1, 2 and 10 in Table 1); (c) TGA and (d) DSC traces of P(N$^R$PenTE) (entries 4, 11−14 and 16−21 in Table 1).

for those PTEs with R = C1/C2, which were only soluble in trifluoroacetic acid (TFA) and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP). Infrared (IR) spectroscopy indicated the formation of hydrogen bonds in side chain urethane groups for all polymers (Fig. 2 and Fig. S45 in ESI).[59,60] It was expected that, when R = C1/C2, the urethane groups were well-exposed and formed intermolecular physical crosslinking via hydrogen bonds, which limited their solubility. As the length of alkyl group increased and the urethane groups were immersed by the long, bulky R groups, both the flexibility of the side chain and the masking effect of intermolecular hydrogen bonds can contribute to the improved solubility of resulting PTEs. Size-exclusion chromatography (SEC) showed that the obtained polymers had moderate dispersity ($Đ$) in the range of 1.05–1.29, with the number-average molecular weight ($M_n$) of 10–30 kg·mol$^{-1}$ for $[M]_0$:[BnSH]$_0$:[DBU]$_0$=100:1:1 (entries 1–11, Table 1) and 40–85 kg·mol$^{-1}$ for $[M]_0$:[BnSH]$_0$:[$^t$BuP$_4$]$_0$=300:1:1 (entry 12–22, Table1). Of note, the sterically hindered N$^{iC3}$PenTL gave a low conversion of 40% and 17% (entries 4 and 15, Table 1), likely due to the increased steric hindrance posed by the branched iC3 side group. On the other hand, the R = C12 side chain rendered the resulting P(N$^{C12}$PenTE) high crystallinity and phase separation, which also adversely affected the polymerization (entries 11 and

22, Table 1).

The thermal properties of P(N$^R$PenTE) were measured by thermogravimetric analysis (TGA, Fig. 2c) and differential scanning calorimetry (DSC, Fig. 2d). Most polymers show good thermal stability with a 5% weight loss decomposition temperature ($T_d$) higher than 220 °C (Fig. 2c). The glass transition temperature ($T_g$) of the polymers were tunable over a wide range of 130–50 °C by changing side chain alkyl length and structure (Fig. 2d). It was proposed that, as the length of alkyl side group increased, the intermolecular hydrogen bonds were more shielded and the proportion of polar segments in the polymer was diluted, which together acted as "internal plasticizers" leading to the gradually decreased $T_g$. From R = C2 to C6, it can be found the $T_g$ of P(N$^R$PenTE) decreased ~10 °C for each addition of carbon in the linear alkyl group (Fig. 2d). On the other hand, when R = C6–C12, P(N$^R$-PenTE) started to exhibit a melting temperature ($T_m$) of about 90–105 °C (Fig. 2d), likely due to the crystallization of side chains.

Next, the condensed structure of P(N$^R$PenTE) were characterized by X-ray diffraction (XRD, Figs. 3a–3c). The amorphous P(N$^{C3}$PenTE) (entry 14, Table 1) was prepared into a hot solution of 1,4-dioxane, and the solvent was slowly evapor-
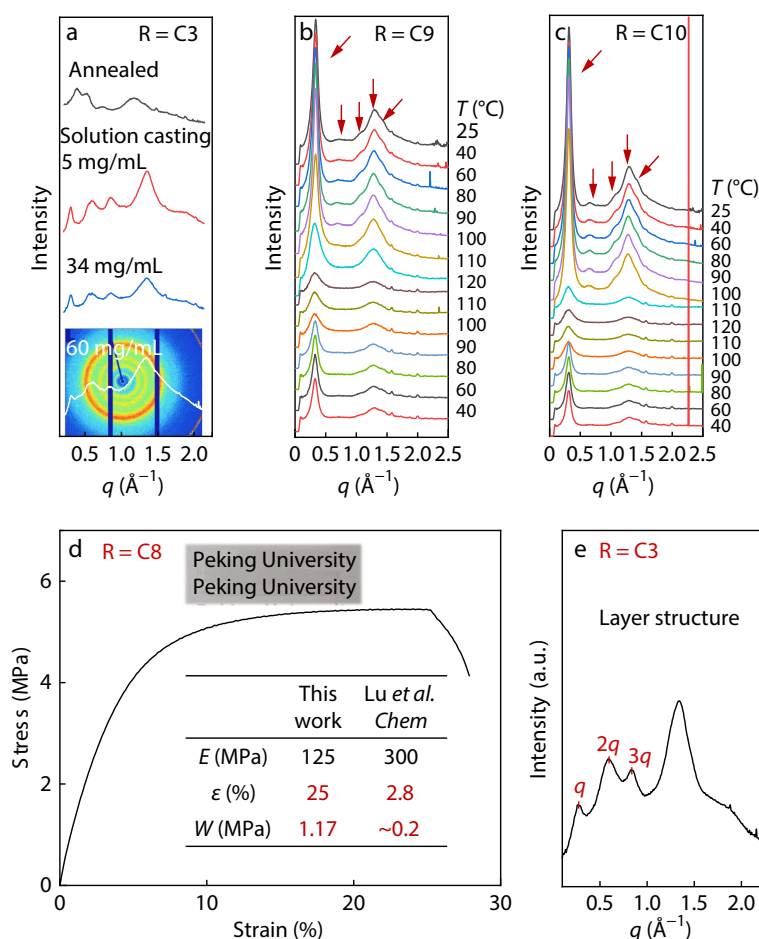


**Fig. 3**　(a) 1D XRD results of P(N$^{C3}$PenTE) (entry 14, Table 1) after annealing and solution (1,4-dioxane) casting measured in the low angle region. Inset: 2D XRD pattern after 60 mg·mL$^{-1}$ solution casting. *In situ* thermal XRD results of (b) P(N$^{C9}$PenTE) (entry 20, Table 1) and (c) P(N$^{C10}$PenTE) (entry 21, Table 1) measured in the low angle region; (d) Tensile test results of *in situ* P(N$^{C8}$PenTE) film and comparison with hot-pressed P(N$^{C8}$PenTE) film in previous work;[22] (e) 1D XRD results of *in situ* P(N$^{C3}$PenTE) film measured in the low angle region.

ated after solution casting. The sample was arranged into an ordered structure and a set of layer diffractions were detected with the first-order one at $q=0.30$ Å$^{-1}$, indicating a layer period of 2.09 nm (Fig. 3a). Unlike P(N$^{C3}$PenTE), the bulk sample of R = C9/C10 (entries 20 and 21, Table 1) exhibits similar small angle diffractions with the 1:2 $q$-ratio, indicating a possible layered structure with a $d$ spacing of 1.90 nm (Figs. 3b and 3c). Although the diffractions in the high angle region were not completely separated (Figs. 3b and 3c, indicated by the arrows), they implied crystalline structures. Moreover, combined with DSC results (Fig. S46 in ESI), the low supercooling required for crystallization was similar to the liquid crystal transition.

Subsequently, polymer films were prepared using high $M_n$ P(N$^{C10}$PenTE) (entry 21, Table 1) by hot pressing. Dynamic mechanical analysis (DMA) demonstrated storage modulus of about 418 and 167 MPa at 30 °C and 60 °C, respectively (Fig. S47 in ESI). The material was viscoelastic, and mainly underwent elastic deformation under test conditions (Fig. S46 in ESI). The maximum tan$\delta$ was at 71.8 °C, suggesting a possible

glass transition process (Fig. S46 in ESI). To improve the toughness of the material and simplify the purification process, we tested the idea of utilizing the unconverted monomers (~20%) in the polymerization system as a plasticizer without separation. Briefly, the initiator and catalyst were mixed with the concentrated N$^{C8}$PenTL monomer solution in THF at 500 mg·mL$^{-1}$ ([N$^{C8}$PenTL]$_0$:[BnSH]$_0$:[$^t$BuP$_4$]$_0$=300:1:1) , which was dropped onto a PTFE film. The reaction proceeded toward polymerization as THF was evaporated, affording a highly transparent film with a thickness of ~0.59 mm (Fig. 3d). Compared to the hot-pressed film of P(N$^{C8}$PenTE) in previous work ($E$=300 MPa, $\varepsilon$=2.8%, $W\approx$0.2 MPa),[22] this monomer-plasticized film showed a significantly improved elongation-at-break (25%) and breaking energy (1.17 MPa), as well as an acceptable Young's modulus (125 MPa) (Fig. 3d). Meanwhile, the *in situ* film of P(N$^{C3}$PenTE) directly developed layered structure with a layer period of 2.35 nm (Fig. 3e).

To modulate material properties, we chose monomers with amorphous short alkyl (R = C4) and crystalline long alkyl (R =

**Table 2**   Ring-opening copolymerization results of N$^{C4}$PenTL and N$^{C12}$PenTL.

| Entry | Base | [C4]$_0$/[C12]$_0$/[I]$_0$/[base]$_0$ | Time (h) | $M_n^{cal\ a}$ (kg·mol$^{-1}$) | $M_n^{obt\ b}$ (kg·mol$^{-1}$) | Đ $^c$ | Conv. $^d$ | [C4]/[C12] $^e$ |
|---|---|---|---|---|---|---|---|---|
| 1 | DBU | 90/10/1/1 | 2 | 24.2 | 14.2 | 1.18 | 64% | 89/11 |
| 2 | DBU | 80/20/1/1 | 2 | 25.4 | 19.8 | 1.27 | 62% | 80/20 |
| 3 | DBU | 70/30/1/1 | 2 | 26.5 | 16.5 | 1.19 | 63% | 69/31 |
| 4 | DBU | 60/40/1/1 | 2 | 27.6 | 18.5 | 1.21 | 63% | 59/41 |
| 5 | DBU | 50/50/1/1 | 2 | 28.7 | 20.0 | 1.12 | 57% | 48/52 |
| 6 | DBU | 40/60/1/1 | 2 | 29.9 | 20.8 | 1.13 | 58% | 40/60 |
| 7 | DBU | 30/70/1/1 | 2 | 31.0 | 19.5 | 1.11 | 58% | 31/69 |
| 8 | DBU | 20/80/1/1 | 2 | 32.1 | 15.0 | 1.28 | 65% | 19/81 |
| 9 | DBU | 10/90/1/1 | 2 | 33.2 | 14.4 | 1.18 | 61% | 9/91 |

All polymerizations were initiated with benzyl mercaptan and conducted in THF at room temperature. $^a$ Calculated number-average molecular weight based on the feeding M/I ratio; $^b$ Obtained number-average molecular weight and $^c$ dispersity determined by SEC in DMF with 0.1 mol/L LiBr; $^d$ Monomer conversion, determined by $^1$H-NMR; $^e$ Molar ratio of R = C4 and C12 in the obtained copolymers, determined by $^1$H-NMR.
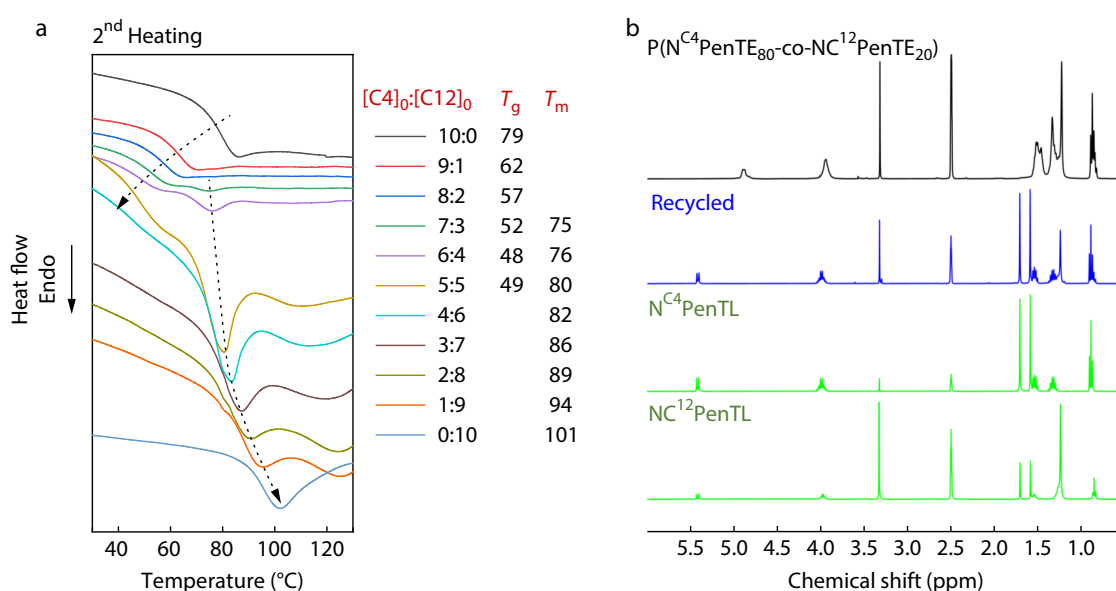


**Fig. 4**   (a) DSC traces of P(N$^{C4}$PenTE-*co*-N$^{C12}$PenTE) (entries 11 and 16 in Table 1; entries 1–9 in Table 2); (b) Overlay of the $^1$H-NMR spectra in DMSO of P(N$^{C4}$PenTE$_{80}$-*co*-N$^{C12}$PenTE$_{20}$) (entry 2 in Table 2), recycled monomers after depolymerization, and the started N$^{C4}$PenTL and N$^{C12}$PenTL as references.

C12) to conduct copolymerizations, obtaining a series of co-polymers with number-average molecular weights of about 14–21 kg·mol$^{-1}$ (Table 2). As the proportion of R = C12 increased, the $T_g$ of the polymers gradually decreased from 79 °C to 50 °C (Fig. 4a). At the same time, when the content of R = C12 was higher than 30%, a melting transition process occurred, and $T_m$ gradually increased from 75 °C to 101 °C (Fig. 4a). The properties of copolymers changed predictably as side chains were altered, demonstrating that copolymerization can effectively regulate material properties. Finally, the recyclability of the end-capped copolymers was investigated (Fig. 4b). P(N$^{C4}$PenTE$_{80}$-*co*-N$^{C12}$PenTE$_{20}$) (entry 2, Table 2) was dissolved in DMSO at 5 mg/mL with 0.7 equiv. of sodium thiophenoxide (PhSNa) relative to the number of converted monomers. After stirring overnight at ambient temperature, the copolymers were completely depolymerized back to initial N$^{C4}$PenTL and N$^{C12}$PenTL, and the recovered monomers can be easily separated and purified by column chromatography (Fig. 4b and Fig. S48 in ESI).

## CONCLUSIONS

In summary, this work successfully synthesized a series of *β*-TL monomers with varied alkyl side groups and studied their ROP behaviors. A preliminary structure-property relationship between the side chain structure and material thermal property was established. Moreover, the material properties were found effectively modulable *via* copolymerization. By virtue of the Thorpe-Ingold effect,[57,58] the chain propagation was highly controlled and the copolymers were completely depolymerizable. The urethane structures in the side chains brought in intramolecular and/or intermolecular hydrogen bonds,[59] making the PTEs with short side chain alkyl groups (R = C1/C2) exhibit excellent solvent resistance and mechanical strength. Given the high reflective index brought by the abundant sulfur elements and the low density of polymers, these materials are expected to be useful as high-value recyclable optical materials,[61,62] which is being explored in our group.

## Conflict of Interests

The authors declare no interest conflict.

## E   Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://doi.org/10.1007/s10118-023-3001-8.

## ACKNOWLEDGMENTS

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