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Rapid synthesis of functional poly(ester amide)s through thiol–ene chemistry†

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Poly(ester amide)s (PEAs) bearing various side chains were synthesized by post-polymerization modification of **PA-1**, a vinylidene containing PEA. The thiols 1-dodecanethiol (1A-SH), 2-phenylethanethiol (1B-SH), 2-mercaptoethanol (1C-SH), thioglycolic acid (1D-SH), furfuryl mercaptan (1E-SH) and sodium-2-mercaptoethanesulfonate (1F-SH) were reacted with **PA-1** to form PEAs **PA-1A** through **PA-1F** respectively. PEAs containing non-polar thiol side chains (**PA-1A**, **PA-1B**, **PA-1E**), showed little change in solubility compared to **PA-1**, while PEAs with more polar side chains improved solubility in more polar solvents. **PA-1F**, functionalized with sodium-2-mercaptoethanesulfonate, became water-soluble. The introduction of pendant functional groups impacted the thermal behaviors of PEAs in a wide range. The PEAs were thermally stable up to 368 °C, with glass transition temperatures (T_g) measured between 117 to 152 °C. Moreover, to demonstrate the versatility of the PEAs, thermal reprocessable networks and polyurethanes were successfully fabricated by reacting with a bismaleimide (1,6-bis(maleimido)hexane, **1,6-BMH**) and a diisocyanate (4,4′-diphenylmethane diisocyanate, **4,4′-MDI**), respectively. This study paves the way for the facile synthesis of functional poly(ester amide)s with great potential in many fields.

Introduction

Poly(ester amide)s (PEAs) are polymers with ester and amide linkages in their polymeric backbone.[1] PEAs combine the good biocompatibility and environmental degradability of polyesters with the high thermal stability and mechanical strength of polyamides. In recent years, these promising materials received increasing attention in various fields, especially in biomedical applications. For example, PEAs have been applied in controlled drug delivery, non-viral gene carriers, hydrogels, and tissue engineering scaffolds.[2–5]

Typical synthetic methods for PEAs are polycondensation or ring-opening polymerization (ROP).[1,5] For instance, Li synthesized a series of semi-aromatic PEAs *via* the ROP of eight-membered cyclic(ester-amide)s in the presence of organocatalysts such as 1,5,7-triazabicyclo[4.4.0]-dec-5-ene (TBD) or 1,8-diazabicyclo[5.4.0]undecane-7-ene (DBU)/thiourea (TU) (Scheme 1a).[6] Loos reported a strategy for the enzymatic polymerization of furan-based poly(ester amide)s. PEAs (M_n up to 4.4 kDa) were successfully synthesized by the polycondensation of dimethyl 2,5-furandicarboxylate (DMFDCA) with aliphatic diols, diamines, or amino alcohols in ionic liquids – $BMIMPF_6$ or $EMIMBF_4$ (Scheme 1b).[7] Other methods like polyaddition of bis(2-oxazoline)s and dicarboxylic acids have also been used for the preparation of PEAs (Scheme 1c).[8] Despite the many merits of these methods, an inert atmosphere is often required for polymerizations, and there are restrictions on the available functional groups in the final polymer.

Aziridines, three-membered heterocycles with ring strain, are versatile and powerful building blocks in polymer synthesis.[9–11] Aziridine and other nonactivated aziridines tend to polymerize *via* chain-growth, cationic ring-opening polymerizations (CROPs), often forming branched structures.[12–14] In contrast, aziridines activated with electron-withdrawing groups on the nitrogen (typically sulfonyl groups), polymerize anionically to form linear polymers, of which many have been reported.[9,10,15–24] Recently, bissulfonyl aziridines are also finding application in step-growth polymerizations. For example, Yoon and Zhang independently reported a series of bis(*N*-sulfonyl aziridine) monomers, which can be polymerized with various dinucleophiles such as dicarboxylic acids, diphenols, dithiols and diamines.[25–29]

We recently reported on chain-growth AROP of carbamate activated aziridines[11] and the step-growth polymerization bis(*N*-carbonyl aziridine)s with dinucleophiles (Scheme 1d).[30] We found that bis(*N*-carbonyl aziridine)s rapidly polymerize with a variety of dinucleophiles, including dicarboxylic acids to produced PEAs.[31–33] These polymerizations were conducted under mild conditions and are very functional group tolerant, allowing the synthesis of highly functional PEAs (e.g., **PA-1** in Scheme 1e).

We propose that **PA-1** (and similar PEAs) can be valuable, sustainably sourced polymers for a wide range of applications.

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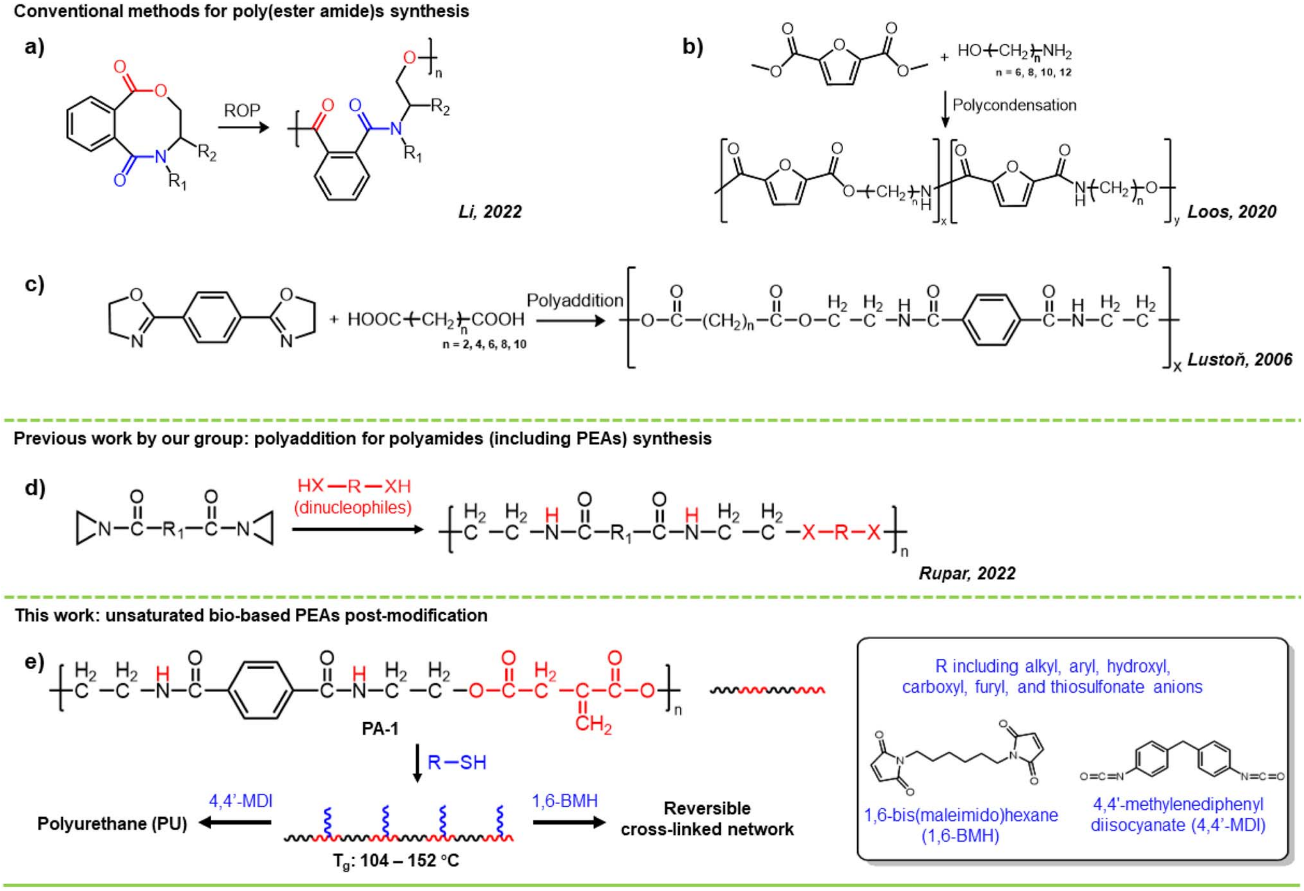


Scheme 1 (a) Ring-opening polymerization for PEAs synthesis; (b) polycondensation for PEAs synthesis; (c) polyaddition for PEAs synthesis; (d) polyamides (including PEAs) prepared by step-growth polyaddition of bis(*N*-carbonyl aziridine)s; (e) unsaturated bio-based PEAs post-polymerization modification (this work).

In this paper, we explore the post-polymerization modification of **PA-1**, which forms from the copolymerization of post-consumer PETE-derived terephthalaziridine (**TP-Az**) and itaconic acid (Scheme 1e). We use thiol–ene chemistry to synthesize a variety of PEAs from the renewably sourced **PA-1**, creating polymers with tunable thermal properties, a thermal reprocessable network, and a polyurethane film (Scheme 1e).

Results and discussion

Thiol–ene couplings are a powerful synthetic tool for the post-polymerization modification of polymers.[34] However, to the best of our knowledge, there are only a few examples of polymerization modification of PEAs using thiol–ene chemistry. Furthermore, the preparation of the parent PEAs in those studies was relatively complicated and only a few thiol reagents were examined for post-polymerization modification.[35,36]

We synthesized a single batch of **PA-1** from the copolymerization of **TP-Az** and itaconic acid for use in this study.[30] **PA-1** was isolated as white power with an M_n of 6.4 kDa, dispersity of 2.08, T_g of 117 °C, and onset of thermal mass loss of 225 °C (Table 1). We next selected a variety of thiols to react with the vinylidene groups of **PA-1**, so to explore the various properties of the resulting PEAs and to introduce new functionalities (Scheme 2). Thiols 1-dodecanethiol and 2-phenylethanethiol were chosen with the anticipation that the introduction of the alkyl and phenyl groups will increase hydrophobicity and improve solubility in non-polar solvents.[37] Next, 2-mercaptoethanol was chosen for its ability to add hydroxyl groups, which could results in a significant change in hydrogen bonding interactions and increases the possibility of further modification reactions, like substitution, elimination, oxidation, *etc.*[38] Similarly, thioglycolic acid, which containing a carboxyl group, may endow PEAs with tunable hydrogen bond strength and coordinative sites for potential applications.[39] Furfuryl mercaptan was then explored as this should allow reversible Diels–Alder reactions, which we intend to use for reversible network formation with bismalemides.[40] Finally, sodium-2-mercaptoethanesulfonate was selected to introduce anionic moieties into the polymer backbones. This was done to study potential differences in solubility and thermal properties of neutral and ionic poly(ester amide)s.[41]

All the thiol–ene reactions with **PA-1** were performed under mild conditions (50 °C, 24 h), without the assistance of any radical initiators or base, to produce **PA-1A** through **PA-1F**. In each case, the desired polymer product was confirmed by ^{1}H NMR spectroscopic analysis (Fig. 1 and S2–S7†). Using the ^{1}H NMR spectrum of **PA-1A** as an example (Fig. 1), the

Table 1 Poly(ester amide) (**PA-1**) post-modifications (thiol–ene click reactions) with various thiol reagents were performed at 50 °C for 24 h

Entry	Polymer	Functional thiol	$M_n{}^a$/kDa	$Đ^a$	Yield (%)	$T_{d,5\%}{}^b$ (°C)	$T_g{}^c$ (°C)
1	**PA-1**	n/a	6.4	2.08	80	225	117
2	**PA-1A**	1-Dodecanethiol	12.7	2.02	76	309	119
3	**PA-1B**	2-Phenylethanethiol	11.4	1.81	70	316	112
4	**PA-1C**	2-Mercaptoethanol	8.3	2.14	89	368	104
5	**PA-1D**	Thioglycolic acid	5.3	3.51	84	249	123
6	**PA-1E**	Furfuryl mercaptan	9.4	2.17	75	267	109
7	**PA-1F**	Sodium-2-mercaptoethanesulfonate	10.3	2.31	79	270	152

[a] Number-average molecular weight (M_n) and dispersity ($Đ$) determined by GPC in HFIP at 35 °C (PMMA calibration). [b] The temperatures at which a weight loss of 5% ($T_{d,5\%}$, °C) of the PEAs are recorded as the decomposition temperatures. [c] Differential scanning calorimetry (DSC) of the synthesized poly(ester amide)s (PEAs). The data from the 3rd heating cycle is reported.

characteristic signals of the vinylidene protons at $\delta = 6.22$ and 5.79 ppm disappeared and signals corresponding to the protons of the long aliphatic chain were observed at 1.37, 1.19, and 0.82 ppm. Other chemical shifts from the ^{1}H NMR spectrum were assigned to different protons of the **PA-1A** backbone. For example, the signals at $\delta = 4.11$ and 3.49 ppm are attributed to the $–CH_2–CH_2–$ linkages in the backbone formed by the ring opening of **TP-Az**. The signal at $\delta = 7.90$ ppm is from the phenylene protons originated from **TP-Az** and the resonance at $\delta = 8.65$ ppm is attributed to the amide proton. The GPC trace for **PA-1A** showed a shift to higher molecular weight compared to **PA-1** ($M_{n,GPC} = 12.7$ kDa, $Đ = 2.02$, Table 1 and Fig. S11†). The estimated molecular weight of **PA-1A** ($M_{n,GPC} = 12.7$ kDa, $n = 23$) is comparable to the calculated molecular weight ($M_{n,GPC} = 10.4$ kDa, $n = 19$) based on the polymerization degree of the parent **PA-1**. Similar increases in the molecular weights of the remaining thiol–ene modified PEAs were also observed (Table 1 and Fig. S11†). These result, together with NMR analysis, suggest that the thiol–ene coupling proceeded quantitatively.

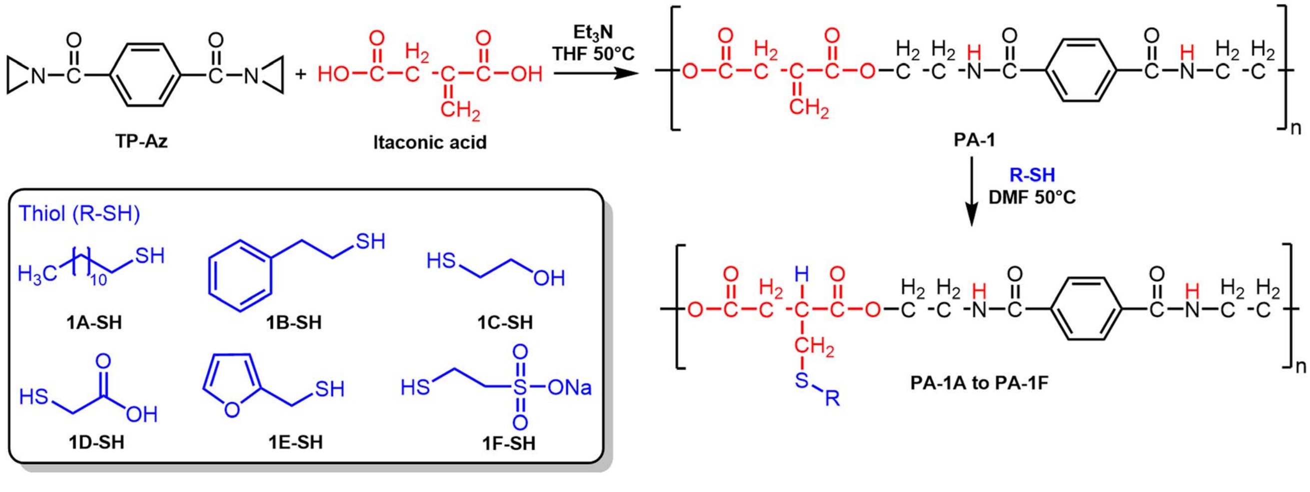
Solubility properties

We observed that the solubilities of the PEAs are impacted by the nature of the thiol–ene grafted side chains. The parent **PA-1** is soluble in DMF, DMSO, and HFIP, but it is insoluble in THF, toluene, DCM, *n*-hexane, methanol, and water. When neutral side chains were added to polymer backbones (*i.e.*, **PA-1A** to **PA-1E**), there was no significant changes in solubility compared to **PA-1**. However, the sodium sulfonate containing **PA-1F** exhibited improved solubility, as it became soluble in methanol and water, in addition to DMF, DMSO, and HFIP.

One basic characteristic of ionic polymers is that the molecular structure contains covalent and ionic bonds. Previous research has explored water-soluble neutral and cationic PEAs,[42,43] but as far as we know, water-soluble anionic PEAs have not been reported before. The changed solubility may allow different processing options and possible applications.

Thermal properties

The thermal properties of poly(ester amide)s **PA-1** and **PA-1A** to **PA-1F** were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The parent polymer (**PA-1**) remained stable to mass loss until 225 °C. All the modified PEAs (**PA-1A** to **PA-1F**) exhibited improved thermal stability with onsets of mass loss ranging from 249 °C to a remarkably high 368 °C (Fig. S8† and Table 1). These data indicated that the addition of pedant groups increased poly(ester amide)s'



Scheme 2 Step-growth polymerizations of **TP-Az** with itaconic acid for **PA-1** synthesis, and thiol–ene click reactions based on **PA-1** with various thiol reagents.

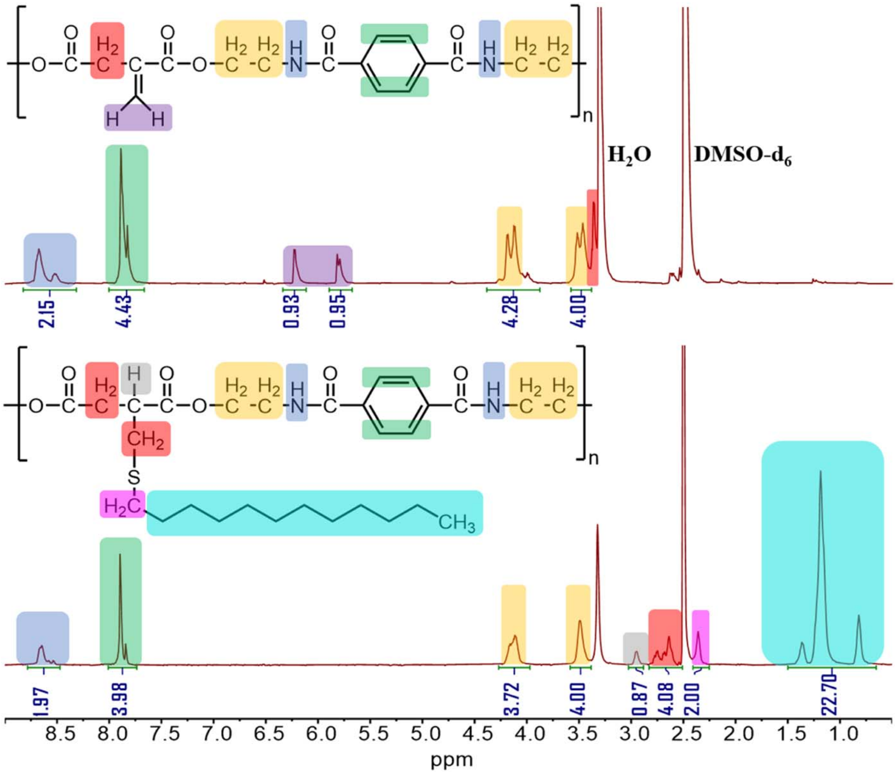


Fig. 1 ^1H NMR spectrum (500 MHz, DMSO-d_6) of poly(ester amide)s **PA-1** (top, the template) and **PA-1A** (bottom, after modification).

thermal stability; similar results have been observed in other polymeric systems modified by thiol–ene click chemistry.[44] The highest decomposition temperature was observed in **PA-1C** (368 °C), which maybe be attributed to the strong inter- and intra-polymer chains hydrogen bonding interaction caused by the hydroxyl substituents. We hypothesize that the relatively poor thermal stability of **PA-1D** (249 °C) is due to the –COOH pendant groups catalyzing chain scission.

The glass transition temperature (T_g) for the parent **PA-1** was measured to be 117 °C by DSC. Upon thiol–ene modification, the T_g of **PA-1A** to **PA-1F** were found to be between 104 to 152 °C. The highest glass transition temperature was observed for the sodium 2-thiosulfonate containing **PA-1F**; anionic moieties are known to increase internal rotation activation energy barriers that can contribute to increased T_g.[45] We observed that the PEAs with non-polar side chains (*i.e.*, **PA-1A**, **PA-1B**, and **PA-1E**), showed very little variation in T_g, suggesting that these side chains do little interrupt in chain packing or that they do not induce internal plasticization. The lowest T_g (104 °C) was observed for the alcohol decorated **PA-1C** (Fig. 2, S10,† and Table 1). According to literature reports, polyols are widely applied as polymer plasticizer.[46–48] The high density of hydroxyl groups in **PA-1C** is likely responsible for the decrease in T_g *via* a similar intermolecular interaction.

As mentioned above, one advantage of poly(ester amide)s over polyesters is superior thermal performance. For instance, the reported T_g of polylactide (PLA) is in a temperature range of 35–60 °C,[49] which is at least 50 °C lower than the T_g of **PA-1** (T_g = 117 °C). As thermoplastics, improved T_g's endow poly(ester amide)s with higher upper temperature limits and better heat resistances. Post-modified poly(ester amide)s with tunable T_g exhibited in this study will further expand the processing window and application field of these polymeric materials.

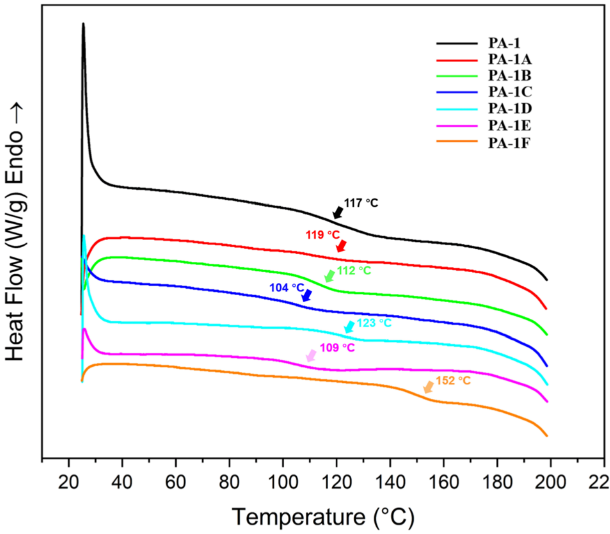


Fig. 2 The DSC curves of PEAs with various pendant thiol groups (heating/cooling rate, 10 °C min^{-1}; under nitrogen). All samples were heated through 3 complete heating/cooling cycles, and the data from the 3rd heating cycle were used for plotting.

Preparation of a PEA-based reversible cross-linked network

Retro-Diels–Alder reactions between dienes and dienophiles are an efficient strategy for reversible cross-linked network formation.[50,51] To illustrate the potential applications of our modified PEAs, a **PA-1E**-based reversible network was prepared *via* a retro-Diels–Alder reaction. 1,6-Bis(maleimido)hexane (**1,6-BMH**, Fig. S8†) was added into a **PA-1E** DMF solution to form a reaction mixture. At room temperature, the viscosity of the mixture progressively increased and within 5 min the medium stopped as the solution gelled. The gel was then heated to 100 °C at which point the mixture became free flowing again with the viscosity becoming like the initial solution after 5 minutes. As shown in Fig. 3, reverse gelation in a covalently cross-linked Diels–Alder poly(ester amide) network was observed by simply changing the ambient temperature. This versatile click–unclick feature undoubtedly contributes to reshaping and reprocessing of the PEAs-based organogel.

Preparation of a PEA-based polyurethane film

Polymers bearing pendant hydroxyl groups are versatile platforms to produce value-added polymeric materials for application in biomedicine, packaging, and others *via* post-polymerization modification.[52–55] Polyurethane **PU** was synthesized *via* reacting **PA-1C** and 4,4′-methylenediphenyl diisocyanate (**4,4′-MDI**) to demonstrate high reactivity of these bio-based hydroxyl-containing poly(ester amide)s (or polyols). The formation of **PU** occurred in two steps: firstly, **PA-1C** was dissolved in a small amount of DMF, followed by mixing **4,4′-MDI** (–NCO : –OH equal to 1 : 1); secondly, the mixture was heated at 120 °C for 30 min to cure. Then DMF was removed under vacuum to afford **PU** as a colorless film. The **PU** film was analyzed by FT-IR to confirm the formation of urethane groups. Fig. 4 shown FT-IR spectra for (a) **PA-1C** (b) **4,4′-MDI** and (c) polyurethane (**PU**) produced by **PA-1C** and **4,4′-MDI**. The **PU** spectrum (Fig. 4c) presented the characteristic bands: the stretching vibration of carbonyl of the carbamate (NCOO) at 1700 cm^{-1}, the deformation vibration of N–H at 1528 cm^{-1}, asymmetric stretching of C–O–C at 1219 cm^{-1} and the symmetric stretching of C–O–C at 1075 cm^{-1}. One broad signal between 3200 to 3600 cm^{-1} is attributed to both stretching vibration of O–H and N–H; this was due to the formation of urethane groups and the remaining –OH groups from **PA-1C**. Other signals corresponding to **PA-1C** (Fig. 4a) were also observed in the **PU** spectrum, as alkyl C–H stretching at 2850–2950 cm^{-1}, and carbonyl ester at 1726 cm^{-1}. Meanwhile, the representative isocyanate vibration attributed to **4,4′-MDI** at 2200 cm^{-1} (Fig. 4b) disappeared in the **PU** spectrum. The FT-IR results indicated that bio-based hydroxyl-containing **PA-1C** synthesized by post-modification of **PA-1** is an appropriate candidate for further reactions like polyurethane (**PU**) production.

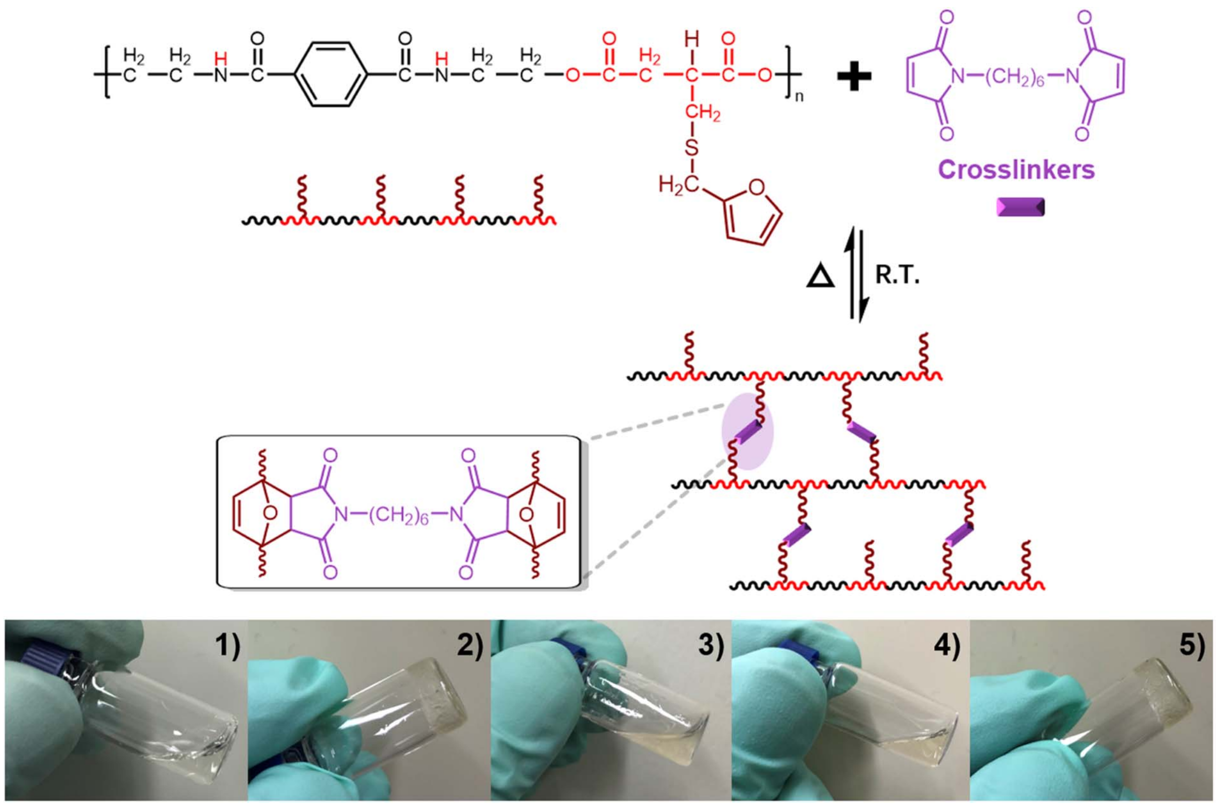


Fig. 3 Top: the retro-Diels–Alder reaction (**rDA**) based on **PA-1E** and 1,6-bis(maleimido)hexane (**1,6-BMH**) for reversible cross-linked polyamide organogel formation; bottom: digital photos of (1) **PA-1E** in DMF; (2) after added **1,6-BMH** for 5 min at room temperature; (3) after heated for 1 min at 100 °C; (4) continue heated for 4 min at 100 °C; (5) cooling to room temperature.

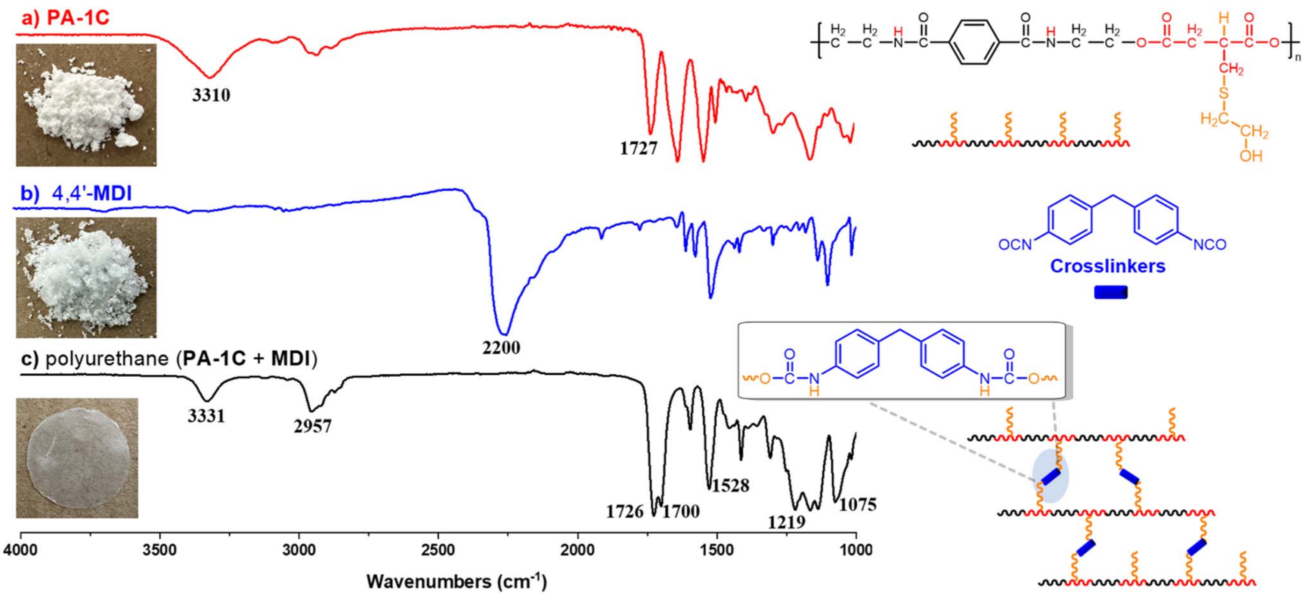


Fig. 4 Comparison of FT-IR spectrum of (a) **PA-1C**; (b) 4,4′-methylenediphenyl diisocyanate (**4,4′-MDI**) and (c) polyurethane (**PU**) produced by a reaction between **4,4′-MDI** and **PA-1C**. The characteristic peaks of the polymers were labeled in the FT-IR spectra.

Conclusions

In conclusion, we have demonstrated a range of synthetic opportunities through the thiol–ene click coupling of bio-derived unsaturated poly(ester amide)s with different thiol reagents. Various pendant functional groups, including alkyl, aryl, hydroxyl, carboxyl, furyl, and sulfonate were successfully incorporated into PEAs backbones for thermal behavior adjustment, thermal reprocessable networks production, and polyurethane film synthesis. Thanks to the simple procedures of the thiol–ene click reaction, all conjugation products were made in good yield. Improved thermal stability and tunable glass transition temperature were observed for modified PEAs compared to the parent, pre-thiol–ene PEA. This ability to routinely prepare functionalized linear PEAs represents an advance compared to traditional approaches and is further evidence of the synthetic utility of click reactions in materials chemistry.

Conflicts of interest

There are no conflicts to declare.

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References

1 M. Winnacker and B. Rieger, Poly(ester amide)s: recent insights into synthesis, stability and biomedical applications, *Polym. Chem.*, 2016, **7**(46), 7039–7046.

2 A. C. Fonseca, M. H. Gil and P. N. Simões, Biodegradable poly(ester amide)s – A remarkable opportunity for the biomedical area: Review on the synthesis, characterization and applications, *Prog. Polym. Sci.*, 2014, **39**(7), 1291–1311.

3 H. Sun, F. Meng, A. A. Dias, M. Hendriks, J. Feijen and Z. Zhong, α-Amino Acid Containing Degradable Polymers as Functional Biomaterials: Rational Design, Synthetic Pathway, and Biomedical Applications, *Biomacromolecules*, 2011, **12**(6), 1937–1955.

4 J. Wu, D. Wu, M. A. Mutschler and C.-C. Chu, Cationic Hybrid Hydrogels from Amino-Acid-Based Poly(Ester Amide): Fabrication, Characterization, and Biological Properties, *Adv. Funct. Mater.*, 2012, **22**(18), 3815–3823.

5 S. Han and J. Wu, Recent Advances of Poly(Ester Amide)s-Based Biomaterials, *Biomacromolecules*, 2022, **23**(5), 1892–1919.

6 Y.-T. Guo, W. Xiong, C. Shi, F.-S. Du and Z.-C. Li, Facile synthesis of eight-membered cyclic(ester-amide)s and their organocatalytic ring-opening polymerizations, *Polym. Chem.*, 2022, **13**(31), 4490–4501.

7 D. Maniar, F. Silvianti, V. M. Ospina, A. J. J. Woortman, J. van Dijken and K. Loos, On the way to greener furanic-aliphatic poly(ester amide)s: Enzymatic polymerization in ionic liquid, *Polymer*, 2020, **205**, 122662.

8 J. Lustoň, J. Kronek, O. Markus, I. Janigová and F. Böhme, Synthesis and polymerization reactions of cyclic imino ethers. 3. Poly(ester amide)s of the AA + BB type on the basis of 2-oxazolines, *Polym. Adv. Technol.*, 2007, **18**(2), 165–172.

9 T. Gleede, L. Reisman, E. Rieger, P. C. Mbarushimana, P. A. Rupar and F. R. Wurm, Aziridines and azetidines: building blocks for polyamines by anionic and cationic ring-opening polymerization, *Polym. Chem.*, 2019, **10**(24), 3257–3283.

10 C. Giri, S. E. Sisk, L. Reisman, I. Kammakakam, J. E. Bara, K. N. West, B. D. Rabideau and P. A. Rupar, Anionic Ring-Opening Polymerizations of N-Sulfonylaziridines in Ionic Liquids, *Macromolecules*, 2022, **55**(2), 623–629.

11 C. Giri, J.-Y. Chang, P. C. Mbarushimana and P. A. Rupar, The Anionic Polymerization of a *tert*-Butyl-Carboxylate-Activated Aziridine, *Polymers*, 2022, **14**(16), 3253.

12 S. Kobayashi, Ethylenimine polymers, *Prog. Polym. Sci.*, 1990, **15**(5), 751–823.

13 M. Jäger, S. Schubert, S. Ochrimenko, D. Fischer and U. S. Schubert, Branched and linear poly(ethylene imine)-based conjugates: synthetic modification, characterization, and application, *Chem. Soc. Rev.*, 2012, **41**(13), 4755–4767.

14 M. L. Sarazen and C. W. Jones, Insights into Azetidine Polymerization for the Preparation of Poly(Propylenimine)-Based CO_2 Adsorbents, *Macromolecules*, 2017, **50**(23), 9135–9143.

15 I. C. Stewart, C. C. Lee, R. G. Bergman and F. D. Toste, Living Ring-Opening Polymerization of N-Sulfonylaziridines: Synthesis of High Molecular Weight Linear Polyamines, *J. Am. Chem. Soc.*, 2005, **127**(50), 17616–17617.

16 J. Xu and N. Hadjichristidis, Well-Defined Poly(Ester Amide)-Based Homo- and Block Copolymers by One-Pot Organocatalytic Anionic Ring-Opening Copolymerization of N-Sulfonyl Aziridines and Cyclic Anhydrides, *Angew. Chem., Int. Ed.*, 2021, **60**(13), 6949–6954.

17 J. Xu, X. Wang and N. Hadjichristidis, Diblock dialternating terpolymers by one-step/one-pot highly selective organocatalytic multimonomer polymerization, *Nat. Commun.*, 2021, **12**(1), 7124.

18 J. Xu, P. Zhang, Y. Yuan and N. Hadjichristidis, Elucidation of the Alternating Copolymerization Mechanism of Epoxides or Aziridines with Cyclic Anhydrides in the Presence of Halide Salts, *Angew. Chem., Int. Ed.*, 2023, **62**(14), e202218891.

19 R. Yang, Y. Wang, W. Luo, Y. Jin, Z. Zhang, C. Wu and N. Hadjichristidis, Carboxylic Acid Initiated Organocatalytic Ring-Opening Polymerization of N-Sulfonyl Aziridines: An Easy Access to Well-Controlled Polyaziridine-Based Architectural and Functionalized Polymers, *Macromolecules*, 2019, **52**(22), 8793–8802.

20 T. Qu and P. A. Rupar, Polymerizations of 2-(Trimethylsilyl) ethanesulfonyl-activated aziridines, *Eur. Polym. J.*, 2022, **169**, 111135.

21 T. Gleede, E. Rieger, J. Blankenburg, K. Klein and F. R. Wurm, Fast Access to Amphiphilic Multiblock Architectures by the Anionic Copolymerization of Aziridines and Ethylene Oxide, *J. Am. Chem. Soc.*, 2018, **140**(41), 13407–13412.

22 C. Bakkali-Hassani, C. Coutouly, T. Gleede, J. Vignolle, F. R. Wurm, S. Carlotti and D. Taton, Selective Initiation from Unprotected Aminoalcohols for the N-Heterocyclic Carbene-Organocatalyzed Ring-Opening Polymerization of 2-Methyl-N-tosyl Aziridine: Telechelic and Block Copolymer Synthesis, *Macromolecules*, 2018, **51**(7), 2533–2541.

23 X. Wang, Y. Liu, Z. Li, H. Wang, H. Gebru, S. Chen, H. Zhu, F. Wei and K. Guo, Organocatalyzed Anionic Ring-Opening Polymerizations of N-Sulfonyl Aziridines with Organic Superbases, *ACS Macro Lett.*, 2017, **6**(12), 1331–1336.

24 H. Wang, J. Li, Z. Li, B. Liu, K. Chen, Z. Zhang, Y. Hu, F. Zhou, Y. Li and K. Guo, Tetrabutylammonium fluoride initiated anionic ring-opening polymerizations of N-sulfonyl aziridines, *Eur. Polym. J.*, 2020, **140**, 109999.

25 S. Kang, H. K. Moon and H. J. Yoon, Diaziridyl Ether of Bisphenol A, *Macromolecules*, 2018, **51**(11), 4068–4076.

26 L. Zhu, H. Huang, Y. Wang, Z. Zhang and N. Hadjichristidis, Organocatalytic Synthesis of Polysulfonamides with Well-Defined Linear and Brush Architectures from a Designed/Synthesized Bis(N-sulfonyl aziridine), *Macromolecules*, 2021, **54**(17), 8164–8172.

27 Z. Zhou, Y. Wang, L. Zhu, D. Dang and Z. Zhang, Tributylphosphine-catalyzed aziridine-based cycloaddition polymerization toward thiacyclic polymers, *Polym. Chem.*, 2022, **13**(33), 4809–4816.

28 S. Chen, L. Zhu and Z. Zhang, Catalyst-free aziridine-based step-growth polymerization: a facile approach to optically active poly(sulfonamide amine)s and poly(sulfonamide dithiocarbamate)s, *Polym. Chem.*, 2022, **13**(29), 4324–4332.

29 Q. Chen, J. Ye, L. Zhu, J. Luo, X. Cao and Z. Zhang, Organocatalytic multicomponent polymerization of bis(aziridine)s, diols, and tosyl isocyanate toward poly(sulfonamide urethane)s, *Eur. Polym. J.*, 2022, **180**, 111585.

30 T. Qu and P. A. Rupar, Carbonyl Aziridines: Strained Amides for Rapid Polyamide Synthesis, *Macromolecules*, 2022, **55**(21), 9513–9519.

31 K. Parkatzidis, H. S. Wang, N. P. Truong and A. Anastasaki, Recent Developments and Future Challenges in Controlled Radical Polymerization: A 2020 Update, *Chem*, 2020, **6**(7), 1575–1588.

32 J. Gopinathan and I. Noh, Click Chemistry-Based Injectable Hydrogels and Bioprinting Inks for Tissue Engineering Applications, *Tissue Eng. Regener. Med.*, 2018, **15**(5), 531–546.

33 X. Wang, Y. Ding, Y. Tao, Z. Wang, Z. Wang and J. Yan, Polycondensation of bis(α-diazo-1,3-dicarbonyl) compounds with dicarboxylic acids: an efficient access to functionalized alternating polyesters, *Polym. Chem.*, 2020, **11**(10), 1708–1712.

34 K. A. Günay, P. Theato and H.-A. Klok, Standing on the shoulders of Hermann Staudinger: Post-polymerization modification from past to present, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**(1), 1–28.

35 X.-X. Deng, L. Li, Z.-L. Li, A. Lv, F.-S. Du and Z.-C. Li, Sequence Regulated Poly(ester-amide)s Based on Passerini Reaction, *ACS Macro Lett.*, 2012, **1**(11), 1300–1303.

36 X.-W. Kan, X.-X. Deng, F.-S. Du and Z.-C. Li, Concurrent Oxidation of Alcohols and the Passerini Three-Component Polymerization for the Synthesis of Functional Poly(ester amide)s, *Macromol. Chem. Phys.*, 2014, **215**(22), 2221–2228.

37 O. Ikkala and G. ten Brinke, Functional Materials Based on Self-Assembly of Polymeric Supramolecules, *Science*, 2002, **295**(5564), 2407–2409.

38 F. Biedermann, E. A. Appel, J. del Barrio, T. Gruendling, C. Barner-Kowollik and O. A. Scherman,

Postpolymerization Modification of Hydroxyl-Functionalized Polymers with Isocyanates, *Macromolecules*, 2011, **44**(12), 4828–4835.

39 O. Ivasenko and D. F. Perepichka, Mastering fundamentals of supramolecular design with carboxylic acids. Common lessons from X-ray crystallography and scanning tunneling microscopy, *Chem. Soc. Rev.*, 2011, **40**(1), 191–206.

40 T. N. Gevrek and A. Sanyal, Furan-containing polymeric Materials: Harnessing the Diels-Alder chemistry for biomedical applications, *Eur. Polym. J.*, 2021, **153**, 110514.

41 D. Chen, C. Cui, N. Tong, H. Zhou, X. Wang and R. Wang, Water-Soluble and Low-Toxic Ionic Polymer Dots as Invisible Security Ink for MultiStage Information Encryption, *ACS Appl. Mater. Interfaces*, 2019, **11**(1), 1480–1486.

42 Y. Lin, J.-W. Gao, H.-W. Liu and Y.-S. Li, Synthesis and Characterization of Hyperbranched Poly(ether amide)s with Thermoresponsive Property and Unexpected Strong Blue Photoluminescence, *Macromolecules*, 2009, **42**(9), 3237–3246.

43 X. Pang, J. Wu, C. Reinhart-King and C.-C. Chu, Synthesis and characterization of functionalized water soluble cationic poly(ester amide)s, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**(17), 3758–3766.

44 E. Esen, P. Hädinger and M. A. R. Meier, Sustainable Fatty Acid Modification of Cellulose in a CO_2-Based Switchable Solvent and Subsequent Thiol-Ene Modification, *Biomacromolecules*, 2021, **22**(2), 586–593.

45 E. A. Campo, 3 - Thermal Properties of Polymeric Materials, in *Selection of Polymeric Materials*, ed. Campo, E. A., William Andrew Publishing, Norwich, NY, 2008, pp 103–140.

46 J. Antoniou, F. Liu, H. Majeed, H. J. Qazi and F. Zhong, Physicochemical and thermomechanical characterization of tara gum edible films: Effect of polyols as plasticizers, *Carbohydr. Polym.*, 2014, **111**, 359–365.

47 M. Rico, S. Rodríguez-Llamazares, L. Barral, R. Bouza and B. Montero, Processing and characterization of polyols plasticized-starch reinforced with microcrystalline cellulose, *Carbohydr. Polym.*, 2016, **149**, 83–93.

48 X. Ma, C. Qiao, X. Wang, J. Yao and J. Xu, Structural characterization and properties of polyols plasticized chitosan films, *Int. J. Biol. Macromol.*, 2019, **135**, 240–245.

49 G. L. Baker, E. B. Vogel and M. R. Smith, Glass Transitions in Polylactides, *Polym. Rev.*, 2008, **48**(1), 64–84.

50 T. Dispinar, R. Sanyal and A. Sanyal, A Diels-Alder/retro Diels-Alder strategy to synthesize polymers bearing maleimide side chains, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**(20), 4545–4551.

51 J. M. Rinehart, J. R. Reynolds and S. K. Yee, Limitations of Diels–Alder Dynamic Covalent Networks as Thermal Conductivity Switches, *ACS Appl. Polym. Mater.*, 2022, **4**(2), 1218–1224.

52 Y. Yu and Y. Chau, One-Step "Click" Method for Generating Vinyl Sulfone Groups on Hydroxyl-Containing Water-Soluble Polymers, *Biomacromolecules*, 2012, **13**(3), 937–942.

53 Y. Xia, D. Zhang, Z. Li, H. Lin, X. Chen, S. Oliver, S. Shi and L. Lei, Toughness modification of cationic UV-cured cycloaliphatic epoxy resin by hydroxyl polymers with different structures, *Eur. Polym. J.*, 2020, **127**, 109594.

54 H. Zhou, Y. Chen, C. M. Plummer, H. Huang and Y. Chen, Facile and efficient bromination of hydroxyl-containing polymers to synthesize well-defined brominated polymers, *Polym. Chem.*, 2017, **8**(14), 2189–2196.

55 P. Alagi, Y. J. Choi and S. C. Hong, Preparation of vegetable oil-based polyols with controlled hydroxyl functionalities for thermoplastic polyurethane, *Eur. Polym. J.*, 2016, **78**, 46–60.