Chinese Journal of
POLYMER SCIENCE

RESEARCH ARTICLE

https://doi.org/10.1007/s10118-025-3321-y
Chinese J. Polym. Sci. **2025**, *43*, 1089–1095

Nucleobase-tackified Thioctic Acid-based Degradable and Recyclable Supramolecular Polymer Adhesives

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Electronic Supplementary Information

Abstract Polymeric materials which can undergo controlled degradation and recycling are of great significance for a sustainable society. Although tremendous progress has been made in the degradation and recycling of both thermoplastic and thermoset plastics, the development of high-performance degradable polymer adhesives is rare. Here, we have prepared high-performance nucleobase-containing thioctic acid-based supramolecular polymer adhesives through free radical polymerization. The specific hydrogen-bonding interactions between complementary nucleobases greatly improve the weak cohesion of the thioctic acid-based polymers and enhance the environmental stability of the thioctic acid-based polymers simultaneously. Degradation of the nucleobase-containing thioctic acid-based supramolecular polymers is achieved by the reduction of the disulfide backbone, and the cycle of degradation and repolymerization is further achieved *via* oxidative polymerization. The adhesion strength of the nucleobase-containing thioctic acid-based supramolecular polymers after two cycles of degradation and repolymerization still reaches as high as 4.7±0.3 MPa. This work provides an approach for the development of environmentally stable and high-performance degradable thioctic acid-based adhesives.

Keywords Thioctic acid; Degradable adhesive; Repolymerization; Nucleobases; Interface

Citation: Wu, J.; Hua, Z.; Liu, G. M. Nucleobase-tackified thioctic acid-based degradable and recyclable supramolecular polymer adhesives. *Chinese J. Polym. Sci.* **2025**, *43*, 1089–1095.

INTRODUCTION

As an indispensable part of modern life, adhesives play a key role in many fields such as construction, packaging, electronics, and medicine.[1–3] However, most of the adhesives currently used are non-degradable and unsustainable polymer adhesives such as polyacrylates,[4–8] polyurethanes,[9–11] epoxy resins[2,12] and EVA emulsion adhesives.[13] Facing with increasingly severe global environmental problems, sustainable development has become an important issue for all industries especially for the production of polymers. In order to tackle the problems arising from polymer plastics, many new biodegradable and sustainable polymer plastics have been developed.[14–17] Biodegradable polymers such as poly(lactic acid) (PLA), polycaprolactone (PCL), poly(butylene adipate-*co*-terephthalate) (PBAT), *etc*. are widely used in the packaging and medical fields.[18,19] They all contain unstable ester bonds in the polymer backbone to enable hydrolysis or microbial degradation. Recently, a supramolecular polyelectrolyte that is degradable using high-salt solutions has also been successfully developed.[20] However, relatively little research has been done on degradable polymer adhesives. A typical example is the copolymerization of acrylates with cyclic ketene acetal (CKA) as a way to introduce cleavable ester bonds in the main chain.[21–23] Despite the appreciable degradability, the large difference in the competing polymerization rates of the two monomers leads to low conversion and non-random incorporation.

Thioctic acid is a naturally occurring small molecule found in plants and animals as an essential coenzyme for aerobic metabolism. Thioctic acid has been shown to undergo ring-opening polymerization under conditions such as heat or light to form polymers with disulfide bonds in the main chain.[24–28] Incorporating disulfide bonds in the main chain, polymers from thioctic acid are easily degraded, recycled, and repolymerized.[25,29,30] Notably, homopolymers from thioctic acid are susceptible to self-degradation due to the unstable free radicals at the end groups, which makes it difficult to use in application scenarios.[31,32] To address the issue, a number of stabilized thioctic acid-based adhesives have been developed using vinyl or polyphenolic compounds to quench the

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Special Topic: Polymers at Interface
Received November 28, 2024; Accepted February 10, 2025; Published online April 10, 2025

end groups.[33,34] Albanese *et al*. constructed a series of degradable acrylic pressure sensitive adhesives by copolymerization of ethyl lipoate and acrylate monomers.[35,36] Recently, a thioctic acid ester monomer with a *N*-hydroxysuccinimide end group has been used in copolymerization of thioctic acid, which is a reliable method for stabilizing thioctic acid-polymers using electrophilic reagents.[37] However, the inherent flexible backbone leads to a low adhesion strength of less than 1.0 MPa, which should be further improved to expedite the practical applicability.

Hydrogen-bonding (H-bonding) interactions between carboxylic acids of the thioctic acid-based polymers themselves are not sufficient to provide adequate cohesion. Meanwhile, some supramolecular interactions have been introduced into thioctic acid-based polymers in order to improve the mechanical properties.[38] For example, thioctic acid-based polymers coordinated with metal ions (Fe^{3+}, Zn^{2+}, Cu^{2+}, Ca^{2+}) have been developed as soft elastomers.[25] The introduction of acylhydrazine H-bonding crosslinked networks into thioctic acid-based polymers can simultaneously enhance the stiffness (by two to three orders of magnitude), toughness, and adhesion of the obtained materials.[39] However, these methods for enhancing the mechanical properties of thioctic acid-based polymers directly through side-chain supramolecular interactions do not take into account the unstable end-groups, leading to possible self-depolymerization of the polymer during use.

Here, we have prepared a series of nucleobase-containing thioctic acid-based supramolecular polymers by copolymerization of acrylate monomers 4-((3-(adenin-9-yl)propanoyl)oxy)butyl acrylate (AAc) and 4-((3-(thymin-l-yl)propanoyl)oxy)butyl acrylate (TAc) with methyl ester of thioctic acid (TAMe), stabilizing the terminal sulfur (S) radicals by carbon (C) radicals with the concomitant introduction of H-bonding interactions in the side chains. The specific H-bonding interactions between complementary nucleobases significantly improve the cohesion of the thioctic acid-based polymers, as evidenced by the fact that the supramolecular polymers with 20 mol% nucleobase have an adhesion strength of 6.7±0.8 MPa. The polymer also shows good stability, achieving an adhesion strength of 5.9±0.3 MPa after one year of bonding in a natural environment. The number-average molecular mass (M_n) of the thioctic acid-based supramolecular polymer with nucleobases is significantly reduced by using dithiothreitol (DTT) reductive degradation from 22.9 kg·mol^{-1} to 4.8 kg·mol^{-1}. The oligomer can be further converted into a high molecular mass polymer again by oxidative polymerization of sulfhydryl groups, giving the adhesion strength of 4.7±0.3 MPa after two times of degradation and repolymerization. This work simultaneously improves the stability and mechanical properties of thioctic acid-based polymers and opens up the possibility of developing high-performance sustainable thioctic acid-based polymers.

EXPERIMENTAL

The experimental sections are detailed in the electronic supplementary information (ESI).

RESULTS AND DISCUSSION

Syntheses and Properties of Nucleobase-containing Thioctic Acid-based Supramolecular Polymers

Thioctic acid-based polymers were synthesized by common radical polymerization using 2,2′-azo-bis-(isobutyronitrile) (AIBN) as the initiator. All synthetic methods of monomers and polymers can be found in the supporting information (Figs. S1–S3 in ESI). Initially, the free radical polymerization of TAMe was investigated, and only about 60% polymerization conversion was obtained by ^{1}H-NMR spectroscopy (Fig. S4 in ESI). This is due to the reversible polymerization-depolymerization of cyclic disulfides, where unstable disulfide bonds lead to low polymerization conversion. Therefore, stabilization of end-group sulfur radicals to mitigate depolymerization is expected to improve the polymerization conversion of cyclic disulfides. When olefinic monomers are introduced into cyclic disulfide polymerization, the combination of carbon and sulfur radicals is able to effectively form stable C—S bonds. The addition of nucleobase-containing acrylate monomers AAc and TAc to TAMe was found to achieve 80% conversion of TAMe (Fig. S5 in ESI). The insertion of C—S bonds effectively prevented the reversible depolymerization of TAMe during polymerization and improved the polymerization conversion of cyclic disulfides.

A series of copolymers P(TAMe$_{(1-2x)}$-*co*-AAc$_x$-*co*-TAc$_x$) (PTAMe and P1–P4) were obtained *via* conventional free radical polymerization with AIBN as the initiator in DMF solution at 75 °C (Table 1), in which 1–2*x*, *x*, and *x* represent the molar ratio of TAMe, AAc, and TAc, respectively. The representative ^{1}H-NMR spectrum of the homopolymer PTAMe has both peaks at 2.79 and 1.99 ppm which were assigned to the protons of the polymer backbone (Figs. 1a and S4 in ESI). When AAc and TAc were added to copolymerize with TAMe, the representative ^{1}H-NMR spectrum of the copolymer P2 has peaks at 12.76, 6.74, and 3.65 ppm, attributing to the proton connected to N3 in thymine, NH_2 in adenine, and CH_3 at the chain end in TAMe, respectively (Figs. 1a and S6 in ESI). In addition, a new emerged peak of extra —S—CH_2— at 2.79 ppm was observed, which was due to the covalent bond between

Table 1 Molecular characterization data of P(TAMe-*co*-AAc-*co*-TAc) copolymers with various nucleobase contents.

Polymer	Structure	M_n [a] (kDa)	$Đ_M$ [a]	T_g [b] (°C)	T_d [c] (°C)
PTAMe	PTAMe	181.1	3.31	–58.1	193.7
P1	P(TAMe$_{0.9}$-*co*-AAc$_{0.05}$-*co*-TAc$_{0.05}$)	18.4	1.42	–14.4	194.4
P2	P(TAMe$_{0.8}$-*co*-AAc$_{0.1}$-*co*-TAc$_{0.1}$)	22.9	1.41	0.8	241.1
P3	P(TAMe$_{0.7}$-*co*-AAc$_{0.15}$-*co*-TAc$_{0.15}$)	30.4	1.49	14.0	252.6
P4	P(TAMe$_{0.6}$-*co*-AAc$_{0.2}$-*co*-TAc$_{0.2}$)	39.4	1.57	18.1	263.1

[a] Determined by DMF SEC with poly(methyl methacrylate) standards. [b] Measured by DSC from the second heating scan from –70 °C to 150 °C at a rate of 10 °C·min^{-1}. [c] Measured by TGA from 40 °C to 700 °C at a rate of 10 °C·min^{-1}; the values represent the 5% degradation point of the copolymers.

https://doi.org/10.1007/s10118-025-3321-y

TAMe and nucleobase-containing monomers. This result illustrates the successful preparation of the copolymer.

Interestingly, the supramolecular H-bonding interaction between adenine and thymine in the copolymers gives rise to a gradual low field shift of the peaks for the protons involving the complementary H-bonding interaction. Specifically, with the molar content of nucleobases increasing from 10% to 40% in the copolymer (P1–P4), the chemical shift of the proton connected to N3 in thymine shifts from 12.5 ppm to 13.0 ppm and NH_2 in adenine from 6.6 ppm to 7.0 ppm (Fig. 1b). This result indicates that the complementary H-bonding interaction is reinforced with higher nucleobase contents in the copolymers. The SEC curve shows that PTAMe has a broad molecular mass distribution (*Đ*) of 3.31, while with the addition of monomers AAc and TAc the molecular mass distributions of copolymers are around 1.50 (Table 1, Fig. S7 in ESI). The conversion of TAMe in P3 increases from 60% to 80% compared to the homopolymer PTAMe (Fig. S5 in ESI). This may be due to the fact that the unstable sulfur radicals are captured by carbon radicals, which reduces the amount of sulfur radicals in the polymerization process. The conversion of the monomer TAMe is improved and the possible broadening of molecular mass distribution due to the high concentration of reactive sulfur radicals was suppressed.

Thermal Analyses of Nucleobase-containing Thioctic Acid-based Supramolecular Polymers

The thermal properties of the obtained copolymers were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Thermal decomposition of the homopolymer PTAMe starts at 193.7 °C due to the instability of the disulfide bonds upon heating. Similarly, the derivative thermogravimetry (DTG) analyses show that the highest decomposition rate reached 258.3 °C for PTAMe. When nucleobases groups are incorporated into thioctic acid-based polymers, the thermal stability of the copolymers is greatly improved. Specifically, when the nucleobase content is gradually increased in the copolymers, the thermal decomposition temperatures of the nucleobase-containing thioctic acid-based copolymers from P1 to P4 are 194.4, 241.1, 252.6, and 263.1 °C, respectively (Fig. 2a and Table 1). Multiple thermal decomposition peaks are observed in the DTG, which should be due to the higher decomposition temperature of the nucleobase components (Fig. S8 in ESI).

The thermal properties of nucleobase-containing thioctic

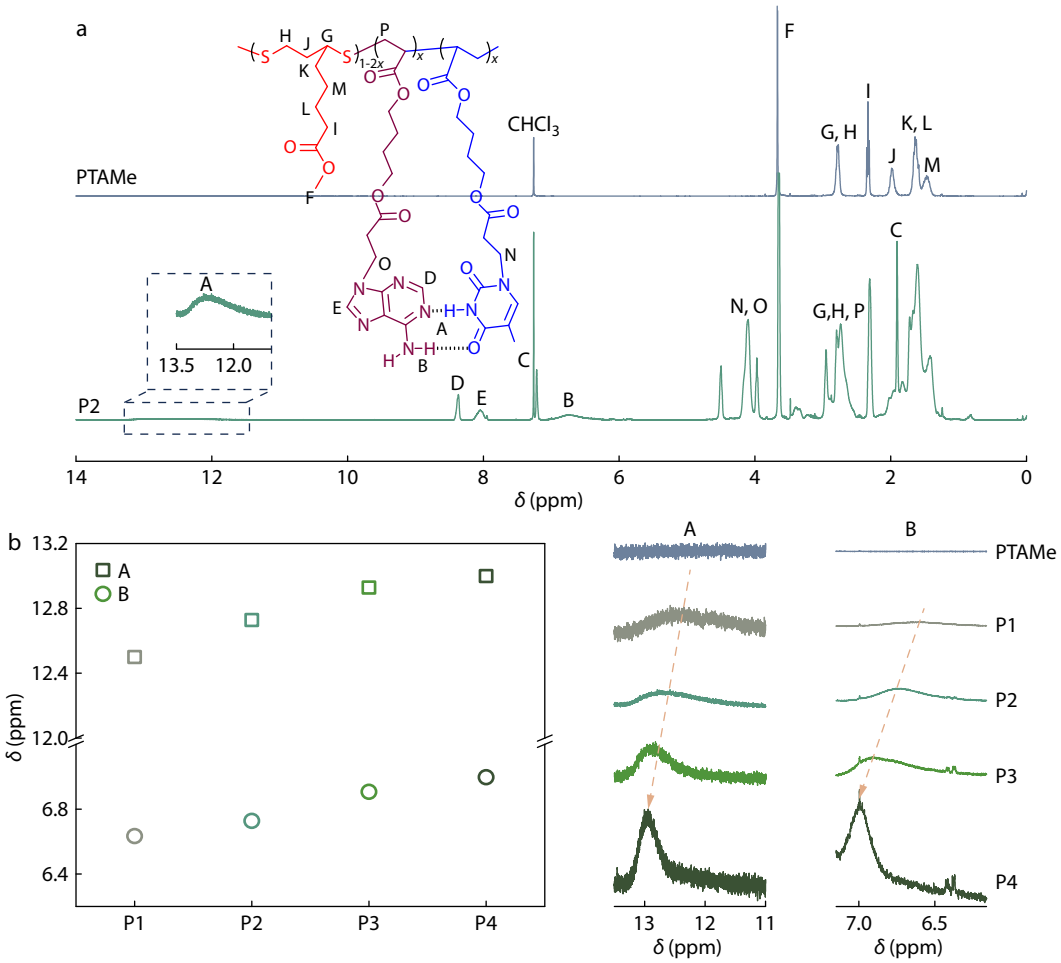

Fig. 1 ^{1}H-NMR spectra of nucleobase-containing thioctic acid-based supramolecular polymers. (a) Representative ^{1}H-NMR spectra of the PTAMe homopolymer and P($TAMe_{0.8}$-*co*-$AAc_{0.1}$-*co*-$TAc_{0.1}$) (P2) copolymer in $CDCl_3$. (b) Chemical shifts change of protons for adenine and thymine involving the complementary H-bonding interaction from P1 to P4.

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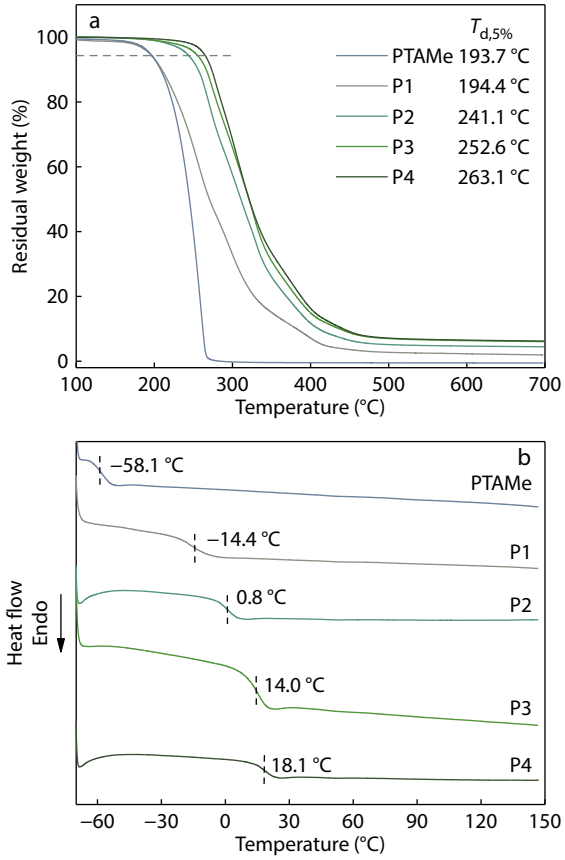

Fig. 2 The thermal analyses of nucleobase-containing thioctic acid-based supramolecular polymers. (a) TGA and (b) DSC thermograms of P(TAMe-*co*-AAc-*co*-TAc) copolymers with different monomer compositions.

acid-based supramolecular copolymers were studied from –70 °C to 150 °C using DSC. The flexible main chains including disulfide bonds and C — C bonds, and flexible side chains result in a glass transition temperature (T_g) of only –58.1 °C for PTAMe. The very low T_g causes PTAMe to present as a fluid state at room temperature and cannot be used as an adhesive. The incorporation of AAc and TAc with rigid nucleobases and specific complementary H-bonding leads to a significant improvement in the T_gs of thioctic acid-based copolymers. The T_g of the thioctic acid-based supramolecular polymer (P1) containing only 10 mol% of nucleobases is –14.4 °C, and with a further increase in the nucleobase contents the T_g of P4 is 18.1 °C (Fig. 2b and Table 1). Specific H-bonding between nucleobases adenine and thymine restricts the chain movement of the polymers, causing significant changes in the T_gs of nucleobase-containing thioctic acid-based supramolecular polymers.

Strong Adhesion of Nucleobase-containing Thioctic Acid-based Supramolecular Polymers

The homopolymer PTAMe contains only low polar groups, resulting in poor intermolecular cohesion and low adhesion to the substrate as an adhesive. It has been demonstrated that the nucleobase components can form multiple interactions with the adhered substrate such as hydrogen bonding, metal complexation, and hydrophobic interactions to improve adhesion. As expected, with an increase in the nucleobase fraction, adhesion and cohesion are simultaneously enhanced, resulting in a strong adhesion. In particular, P2 has the highest adhesion strength of 6.7±0.8 MPa on stainless steel substrate. Higher nucleobase contents lead to a decrease in adhesion strengths, presenting 4.2±0.2 and 4.0±0.5 MPa for P3 and P4, respectively (Fig. 3a). The decrease in adhesion strength of the copolymers with more nucleobases may be caused by the higher glass transition temperature. The high glass transition temperature indicates the chain rigidity of the polymer, and the chain movement of the polymer is limited even under the condition of heating. The unique property makes the adhesive difficult to wet on the substrate, giving rise to poor adhesive performance.

The uncontrolled degradation of polymeric materials at ambient conditions drastically compromises their potential applicability. In order to explore the stability of the adhesive, the nucleobase-containing thioctic acid-based supramolecular polymer adhesive P2 was first stored for one year in a natural environment. Further, the adhesion strength of P2 was evaluated *via* shear test, still achieving the adhesive strength of as high as 5.9±0.3 MPa (Fig. 3b). This result indicates the good shelf life of the nucleobase-containing thioctic acid-based supramolecular polymer adhesive, demonstrating the outstanding stability of the nucleobase-containing thioctic acid-based supramolecular polymers in the environment.

Degradation and Repolymerization of Nucleobase-containing Thioctic Acid-based Supramolecular Polymers

Multiple disulfide bonds in the main chain offer the possibility of degradation for supramolecular polymers. By employing DTT as the reducing agent of the disulfide bond, we achieved a successful degradation of a nucleobase-containing thioctic acid-based supramolecular polymer (Fig. 4a). SEC curve showed that P2 was reduced by DTT to a degraded oligomer (dP2) with a M_n of 4.8 kg·mol^{-1} (Fig. 4b). The oligomer is a polymer fragment with a C—C bond in the main chain formed by acrylate monomers AAc and TAc in random copolymerization, where the end group is a sulfhydryl group from which the disulfide bond is reduced. The reactivity ratio of TAc and TAMe copolymerization was determined at a low polymerization conversion (r_{TAc}=0.98, r_{TAMe}=0.68) (Table S1 and Fig. S9 in ESI). The slightly higher reactivity of acrylate monomer TAc than TAMe should be conducive to the formation polymer fragments of the C—C backbone during copolymerization. This is consistent with the generation of short oligomers after degrading the copolymers.

Further, the attained oligomer is repolymerized to generate a macromolecule (rP2-1) with M_n of 20.9 kg·mol^{-1} by oxidative polymerization of sulfhydryl groups catalyzed by I_2 and pyridine. The degradation and repolymerization cycle could be achieved at least twice (Fig. 4b). The thermal properties of the repolymerized polymers are investigated by DSC, and after two degradations and repolymerization the T_g of P2 increases from 0.8 °C to 14.3 °C (Fig. 4c). This is due to the fact that a portion of the TAMe that depolymerized into small molecules was removed during the purification process after degradation. This leads to an increase in the content of nucleobases in the polymer that was repolymerized (Fig. S10 in ESI). The polymers subjected to two degradations and repolymerization are still able to achieve an adhesion strength of 4.7±0.3 MPa (Fig. 4d).

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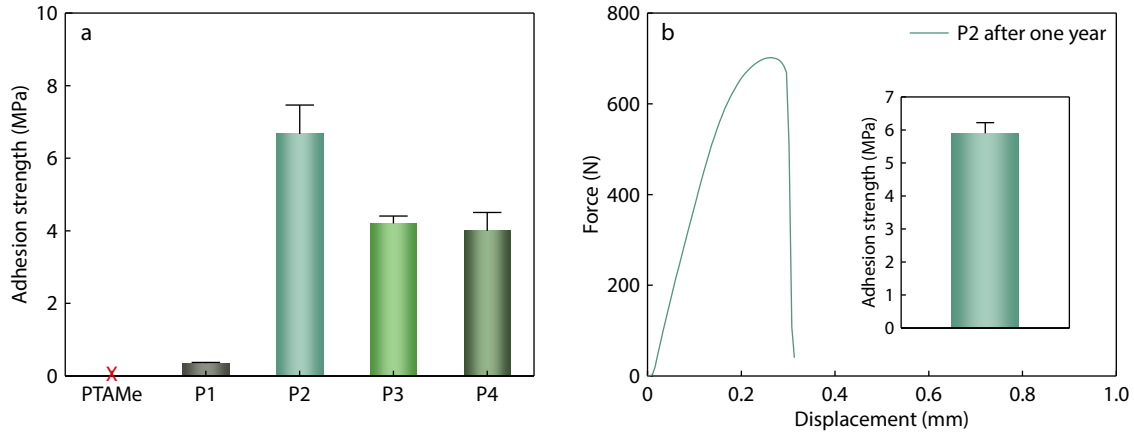

Fig. 3 (a) The adhesion strength of nucleobase-containing thioctic acid-based supramolecular polymers. (b) The adhesion strength of P2 after one year in natural environment. (The adhesion substrate is stainless steel with an adhesion area of 1.25 cm^2.)

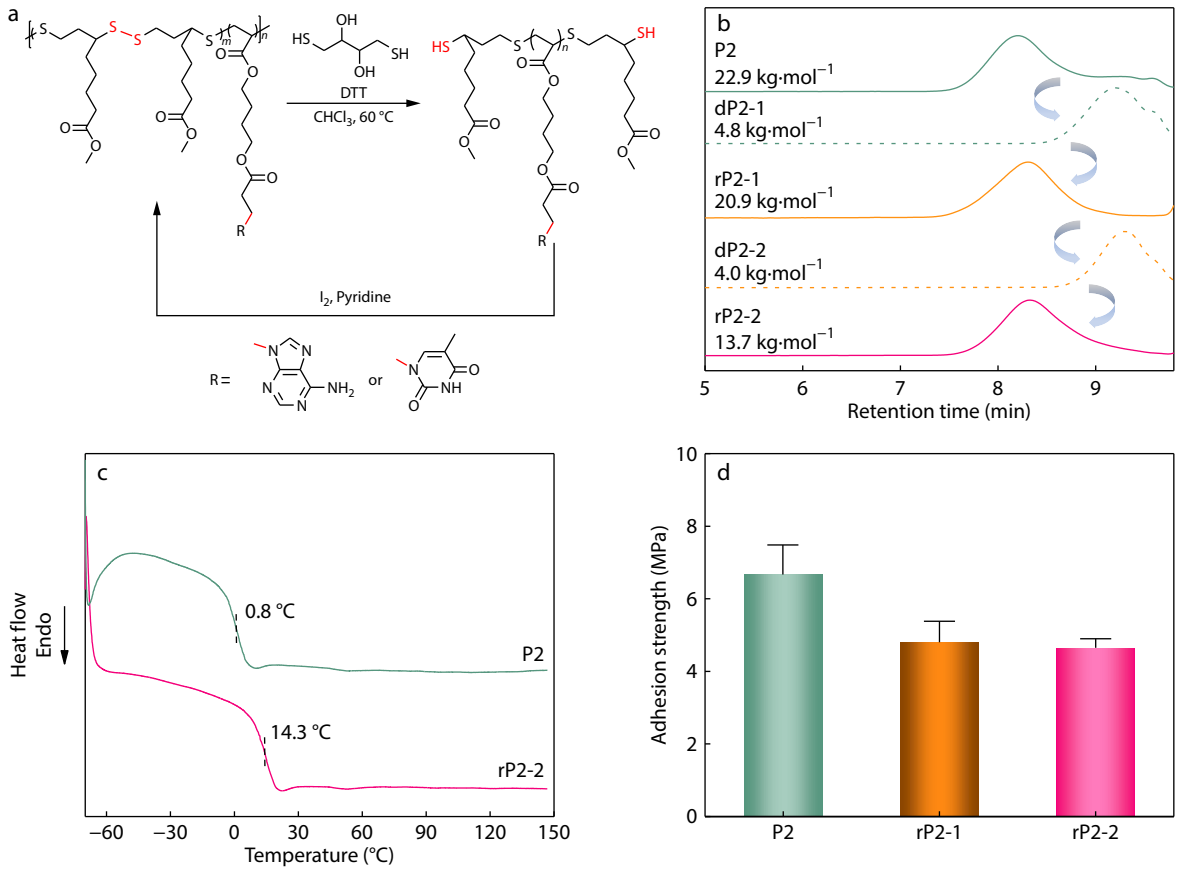

Fig. 4 Degradation and repolymerization of nucleobase-containing thioctic acid-based supramolecular polymers. (a) Schematic representation of the degradation and repolymerization of P2. (b) DMF SEC traces, (c) DSC thermograms and (d) adhesion strength of P2 and repolymerized polymers. dP2-1, dP2-2 and rP2-1, rP2-2 represent the first and second degradation and the first and second repolymerization of P2, respectively.

CONCLUSIONS

In summary, we have prepared a series of nucleobase-containing thioctic acid-based supramolecular polymer adhesives by using free radical polymerization. Specific hydrogen bonding interactions between complementary nucleobases were confirmed by proton NMR spectroscopy. The thioctic acid copolymer with 20 mol% nucleobases possessed the highest adhesion strength of 6.7±0.8 MPa, and its adhesion strength remained 5.9±0.3 MPa after one year in the natural environment, demonstrating its environmental stability. Further controlled degradation of the polymer was achieved by DTT reduction of the backbone disulfide bonds, with M_n changing from 22.9 kg·mol^{-1} to 4.8 kg·mol^{-1}. The repolymerization was achieved by oxidative polymerization, and the adhesion strength of the nucleobase-

https://doi.org/10.1007/s10118-025-3321-y

containing thioctic acid-based supramolecular polymers after two degradation-repolymerization cycles could still reach 4.7±0.3 MPa. This work reports an effective method towards advancing degradable and recyclable polymer adhesives with robust properties.

Conflict of Interests

The authors declare no interest conflict.

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/s10118-025-3321-y.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 22273098, 22373003, 22103002 and 52033001) and the Key Project of Anhui Province Science and Technology Innovation Platform (No. 202305a12020030). Z. Hua also acknowledged the financial support from the Anhui Provincial Natural Science Foundation (No. 2408085Y004). This work was partially carried out at the Instruments Center for Physical Science, University of Science and Technology of China.

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https://doi.org/10.1007/s10118-025-3321-y