

Synthesis of poly(thiourethane-*alt*-thioester) by alternating ring-opening copolymerization of *N*-thiocarboxyanhydrides and episulfides

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Polythiourethanes (PTU) and polythioesters (PTE) derived from renewable sources are emerging sustainable polymers for their excellent degradability and recyclability. However, P(TU-*alt*-TE) copolymers have been rare and challenging to synthesize. Here, we report the efficient synthesis of novel P(TU-*alt*-TE) copolymers *via* the alternating copolymerization of *N*-thiocarboxyanhydrides (NTA)/episulfides (ES) and provide mechanistic insight into the alternating chain propagation process *via* density functional theory (DFT) calculation. The incorporation of ESs into traditional peptide backbone is capable of adjusting the glass transition temperature below thermal decomposition temperature, which confers better thermal processability by regulating the rigidity of the backbone and the hydrogen bond interaction among the polymer chains. Crosslinked PTUs with tailored properties are accessible by altering the feeding ratio of NTAs and (bifunctional) ESs. Moreover, the thiourethane in the backbone can endow interesting underwater adhesion properties to the materials. Considering the broad scope of NTA and ES monomers, this method is expected to provide a promising and general route to a wide range of P(TU-*alt*-TE) copolymers with diverse properties.

poly(thiourethane-*alt*-thioester), alternating, ring-opening copolymerization, *N*-thiocarboxyanhydrides, episulfides

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1 Introduction

Petroleum-based plastics play an important role in social life with their advantages of low cost, easy processing, and portability. However, most of the traditional plastics are non-degradable and non-renewable, and the accumulation of plastic wastes has imposed global environmental crises and resource depletion [1]. To address these challenges, one appealing approach is to develop plastics from renewable biomass-based resources such as carbohydrates, terpenes, vegetable oils, lignin [2–6]. For instance, fine chemicals

derived from these renewable sources are converted into polymerizable monomers and successively transformed into polymers through either step growth condensation/addition reactions, or ring-opening polymerizations (ROP) [7–22].

As a kind of renewable source, α -amino acids have attracted considerable attention for their versatile structures, multivalency, well-defined optical activity, environmentally benign, and biological safety. Previously, amino acids have been exploited to construct various degradable functional materials such as polypeptides [23–25] (a.k.a. poly(amino acid)s), polyurethanes, polyesters [26–28], polythioesters (PTE) [29–35], and polydisulfides [36]. Perhaps the most famous examples are the synthesis of polypeptides through

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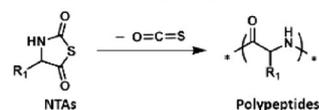
the ROP of the cyclic α -amino acid *N*-carboxyanhydrides (NCA) [37–40] or *N*-thiocarboxyanhydrides (NTA) [41–44]. By harnessing the unique secondary structures of polypeptides [45,46], fascinating crystalline, mechanical, and thermal properties that stem from the well-defined intra/intermolecular hydrogen bonding in the mainchain can often be obtained. However, these unique features are sometimes a double-edged sword, as excessive hydrogen bonding often results in poor processability. Moreover, the degradability of polypeptides, which usually relies on enzymes and microbials, needs to be finetuned for certain applications. Overall, to meet the growing demand for sustainability, there is a strong motivation to develop new chemistry of amino acid-based monomers for high-performance and degradable new materials.

During the ring-opening process of NTA, a synergetic dethiocarboxylation step occurs to ensure the chain growth *via* the α -amine and the successive generation of amide linkage in the main chain (Figure 1a). We envision that if the dethiocarboxylation step can be inhibited, new types of polymers bearing thiourethane functionalities in the main chain could be generated, which may possess improved processability. However, the dethiocarboxylation is generally considered to be favorable, posing a significant challenge to achieving our envision. Fortunately, Lu and Ren [47] previously reported the alternating ring-opening copolymerization (ROCOP) of cyclic thioanhydrides and episulfides, which produced polythioesters with excellent degradability. Inspired by this seminal study and noticing the structural similarity of NTA with cyclic thioanhydrides, we hypothesize that NTA and episulfides might be able to undergo alternating ROCOP without dethiocarboxylation, generating poly(thiourethane-*alt*-thioester) (P(TU-*alt*-TE)) in an unprecedented, efficient fashion (Figure 1b). Such materials may enjoy the backbone thiourethane hydrogen bonding and, in the meantime, with excellent solubility tunable thermal properties owing to the insertion of episulfides and side chain chemical diversity. Moreover, both thiourethane and thioester functionalities are highly dynamic and exchangeable under mild conditions, making them appealing for various recyclable thermoplastic and thermoset materials [48–51].

2 Results and discussion

To begin with, we chose phenylalanine NTA (Phe-NTA) and propylene sulfide (Me-ES) as our modal monomers of ROCOP because the ROP of PheNTA alone would produce polyphenylalanine that is insoluble in almost any solvent (entry 1, Table 1). In this fashion, the unsuccessful ROP could be facily ruled out by the naked eye. By using Me-ES, a liquid monomer, no extra solvent was needed because

(a) ROP of *N*-thiocarboxyanhydrides (NTAs)



(b) This work: ROCOP of NTAs and ESs

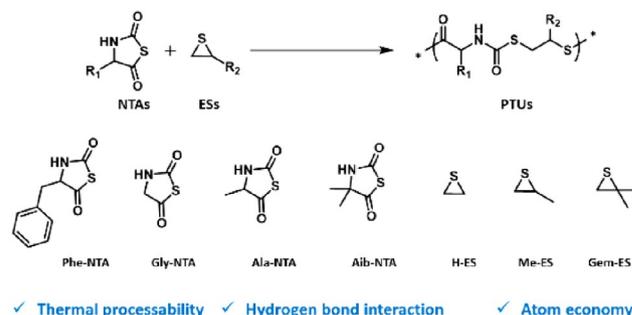


Figure 1 (a) ROP of NTAs and synthesis of polypeptides. (b) The synthesis of poly(thiourethane-*alt*-thioester) from the ROCOP of NTAs and episulfides (color online).

Phe-NTA was dissolved in Me-ES well. We tested the combined use of benzyl mercaptane (BnSH) with 1,8-diazabicyclo[5.4.0]undecane-7-ene (DBU) as an initiation system, which has been widely used for the ROP of various cyclic thiolactone monomers. Upon complete monomer consumption, the viscosity of the system increased significantly but without visible precipitation after the reaction, suggesting no homopolymerization of NTA (entry 2). Signals attributable to both NTA and Me-ES, as well as the absorbance band of thioester bond, were presented in the proton nuclear magnetic resonance (^1H NMR) and Fourier transform infrared spectrometer (FTIR) spectroscopy of the purified product, denoted as p(Phe-MeES) (Figure S1, Supporting Information online). When the polymerization was quenched before NTA was fully consumed, the resulting polymer gave almost 1/1 molar ratio of PheNTA and Me-ES in the ^1H NMR spectrum (Figure 2A), despite an exceedingly disproportional feeding ratio of the two monomers. Notably, the ^{13}C NMR spectrum of this polymer showed two types of carbonyl groups (Figure 2B) originated from Phe-NTA with chemical shifts of ~ 168 and ~ 199 ppm, respectively, which supported the notion of dethiocarboxylation inhibition. To further confirm the alternating ROCOP, the heteronuclear multiple bond correlation (HMBC) spectra demonstrated a strong coupling correlation between the carbonyl (h) at ~ 168 ppm and the hydrogen atoms of the methylene group (f) at ~ 3.1 ppm, as well as the carbonyl (g) at ~ 199 ppm and the methine group (g) at ~ 3.7 ppm (Figure 2C). This conclusion was further supported by matrix-assisted laser desorption/ionization time of flight (MALDI-ToF) mass spectrometry, in which the difference between the adjacent molecular ion peaks was found to be ~ 281.02 g/mol, exactly the sum of the molar mass of Phe-NTA and Me-ES (Figure

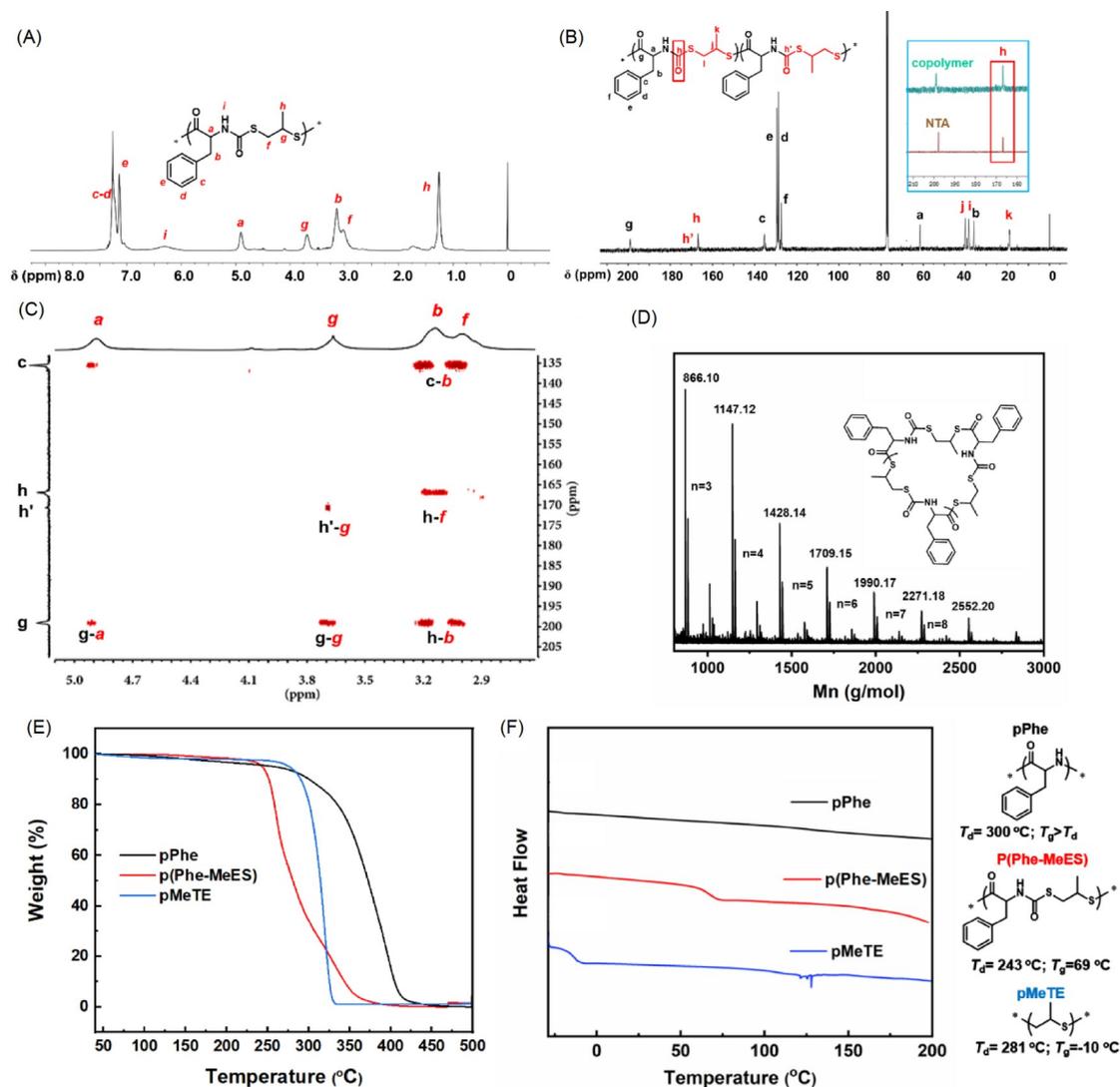


Figure 2 Characterizations of the ROCOP of PheNTA and Me-ES. (A) ^1H NMR, (B) ^{13}C NMR, (C) HMBC, (D) MALDI-TOF spectrum of p(Phe-MeES). (E) TGA and (F) DSC curves of p(Phe-MeES), pPhe, and pMeTE (color online).

2D). Next, the thermal properties of the polythiourethane were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). As illustrated in Figure 2E, the polymer exhibited good thermal stability with a thermal decomposition temperature ($T_{d5\%}$) of ~ 243 °C. As mentioned by Numata *et al.* [52], many polypeptides are challenging to heat process because their melting temperature/glass transition temperature (T_m/T_g) is even higher than their T_d , which was found to be exactly true for the polypeptide pPhe (Figure 2E, F). Interestingly, the T_g of the P(TU-*alt*-TE) copolymer p(Phe-MeES) can be adjusted to ~ 69 °C, which gave a broad heat processing window of the material (Figure 2F). Together, the above results confirmed the alternating ROCOP of NTAs and episulfides without dethiocarboxylation, affording poly(thiourethane-*alt*-thioester) as we initially designed.

To obtain molecular insight of the alternating selectivity,

we calculated the free energy of important intermediates (INT) and transition states (TS) in the ROCOP process, as well as the dethiocarboxylation step in the ROP of NTA as a competitive reaction (Figure 3), using density functional theory (DFT). To simplify the calculation, we used Gly-NTA and propylene sulfide as model monomers, methylamine as initiator, and DBU as catalyst. It was found that, starting from the thiourethane intermediate (INT_0), the free energy of the transition state for the NTA homopolymerization (TS_3) was ~ 1.38 kcal/mol higher than that of the alternating polymerization transition state (TS_1) opening the ring of episulfide, which generated the thiol/DBU intermediate (INT_2). This was further enhanced by the excessively high equivalent of propylene sulfide in the experimental setup. Of note, even though the energy barrier for the direct dethiocarboxylation from INT_0 to generate an amine (INT_{12}) was low, the free energy difference of this process was found

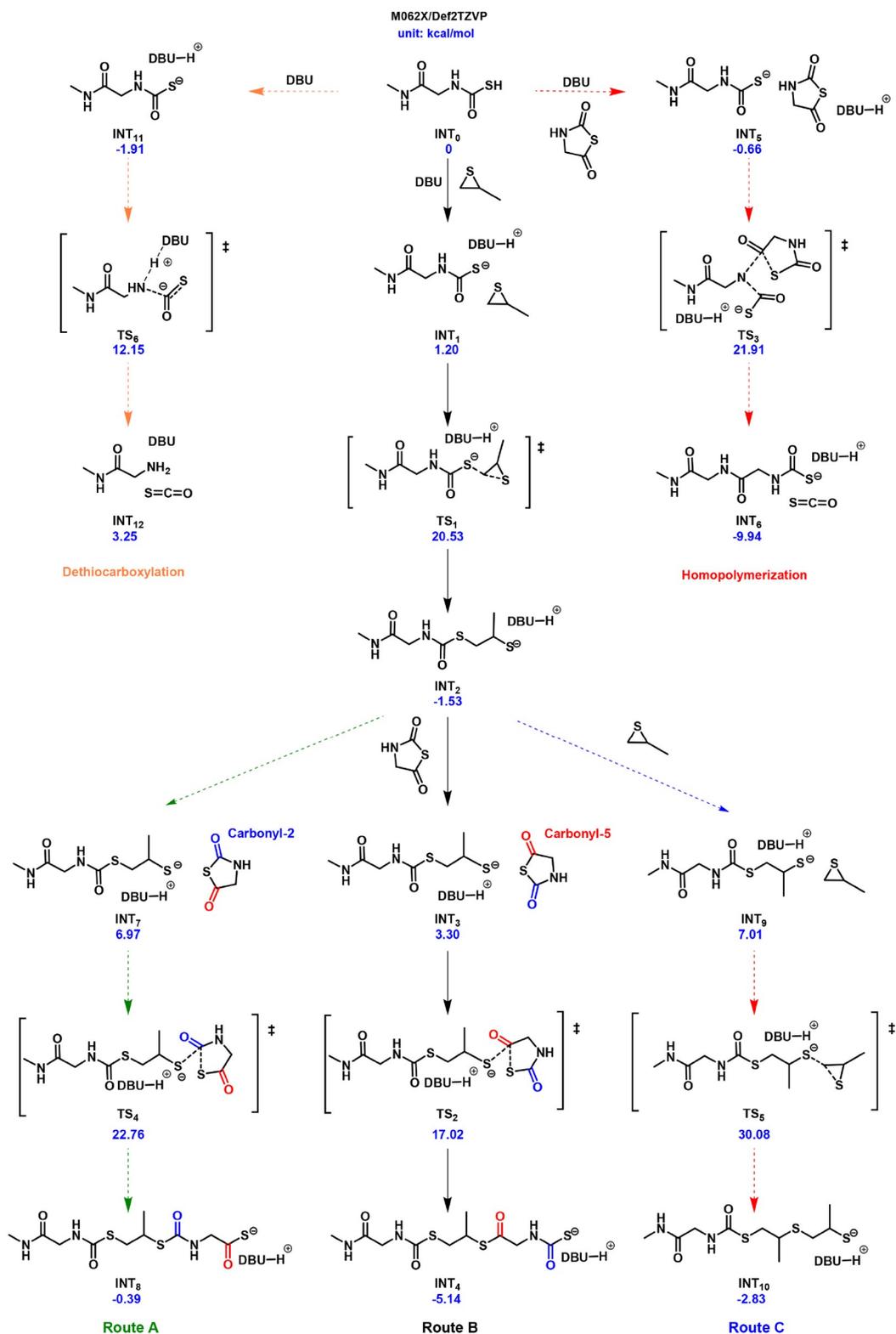


Figure 3 Free-energy profiles for the ring-opening process of NTA and propylene sulfide initiated by active chain end (color online).

thermodynamically unfavored, ~ 3.25 kcal/mol. This implies that a fast equilibrium between INT₀ and INT₁₂ might exist, but it is highly favorable to the former. Once INT₂ was

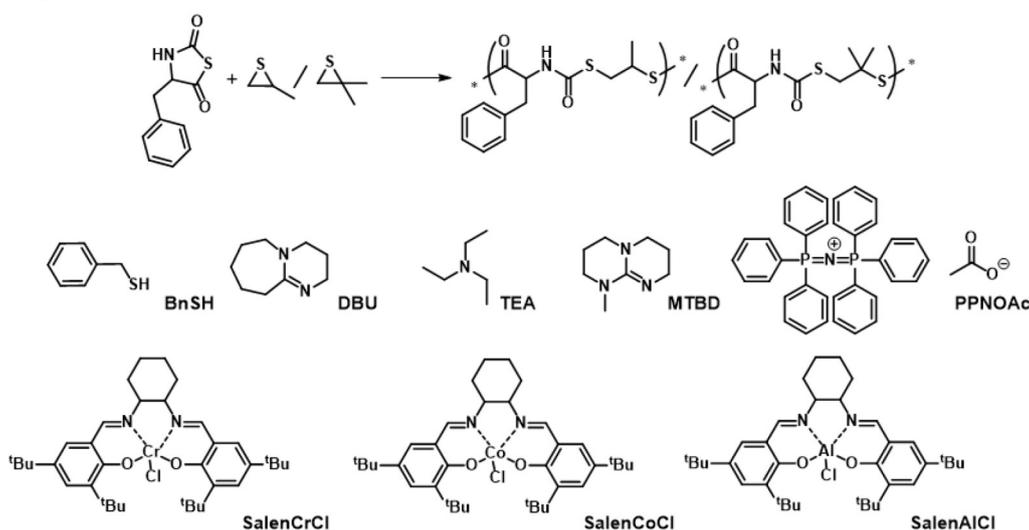
generated, it could attack NTA at either the carbonyl 2 (route A) or carbonyl 5 (route B) of NTA, or react with another episulfide corresponding to the homopolymerization of epi-

sulfide (route C). It was found that, the energy barrier of route B (TS₂) was ~5.74 and ~13.06 kcal/mol lower than that of route A (TS₄) and route C (TS₅), respectively. Overall, the DFT results also supported the preference for alternating polymerization over homopolymerizations of NTA or ep-sulfide.

Having established the alternating sequence of the ROCOP, we sought to screen catalysts to optimize the MW control of the obtained PTU-*co*-PTE. The BnSH/DBU system gave an unsatisfactorily low M_n ~2,830–4,970 g/mol (entries 2–4, Table 1), despite the complete conversion of Phe-NTA monomer. Moreover, even though the size exclusion chromatography (SEC) peak was unimodal (Figure S2),

the dispersity (D) was found to be 1.60–2.08. Conducting the polymerization at a lower temperature (*e.g.*, –20 °C) resulted in only 10% conversion of NTA after 24 h (entry 5, Table 1). Weaker bases such as TEA ($pK_a^{\text{DMSO}} = 9.0$) gave a NTA conversion of ~95% after 48 h, but only led to the production of polymers with a M_n of ~2,770 g/mol (entry 6, Table 1). Other organocatalysts such as bis(triphenylphosphoranylidene)ammonium (PPN) and organometallic catalysts such as [(Salen)CoIII] and [(Salen)CrIII], which previously showed excellent controllability and alternating selectivity for the ROCOP of cyclic thioanhydrides/ep-sulfides or *meso*-epoxides/carbonyl sulfide [53,54], all failed to give a satisfactory M_n in the ROCOP of NTA/ES (entries

Table 1 Ring-opening copolymerization of Phe-NTA and Me-ES/Gem-ES^{a)}



Entry	Initiator	Catalyst	ES	[NTA] ₀ /[ES] ₀ / [I] ₀ /[base] ₀	Time (h)	M_n^{obt} (g mol ⁻¹) ^{b)}	$D^{\text{c)}$	Conv. ^{d)} (%)
1	BnSH	–	Me	50/–/1/–	48	–	–	–
2	BnSH	DBU	Me	50/500/1/1	12	4970	1.69	> 95
3	BnSH	DBU	Me	100/1000/1/1	24	3870	1.60	> 95
4	BnSH	DBU	Me	200/2000/1/1	48	2830	2.08	> 95
5 ^{e)}	BnSH	DBU	Me	50/500/1/1	24	1430	1.53	10
6	BnSH	TEA	Me	50/500/1/1	48	2770	1.67	> 95
7	PPNOAc	–	Me	250/1000/1/–	18	4600	2.81	74
8	PPNOAc	MTBD	Me	250/1000/1/1	18	5300	2.10	> 95
9	PPNOAc	MTBD	Me	250/1000/1/1	1.5	3100	2.45	60
10	SalenCrCl	MTBD	Me	500/500/1/1	30	4100	2.32	87
11	SalenCoCl	MTBD	Me	500/500/1/1	30	4200	2.48	91
12	SalenAlCl	MTBD	Me	500/500/1/1	30	7000	1.94	> 95
13	BnSH	DBU	Gem	100/500/1/1	120	2780	–	> 95
14	PPNOAc	MTBD	Gem	100/500/1/1	120	4360	1.43	>95

a) ROCOP was performed at 25 °C in tetrahydrofuran (THF) under bulk condition. b) Obtained MW. c) Determined by SEC-MALLS analysis in *N,N*-dimethylformamide (DMF). d) Determined by ¹H NMR. e) ROCOP was performed at –20 °C. The monomer utilized in entries 1–12 is MeES, whereas GemES is employed in entries 13, 14.

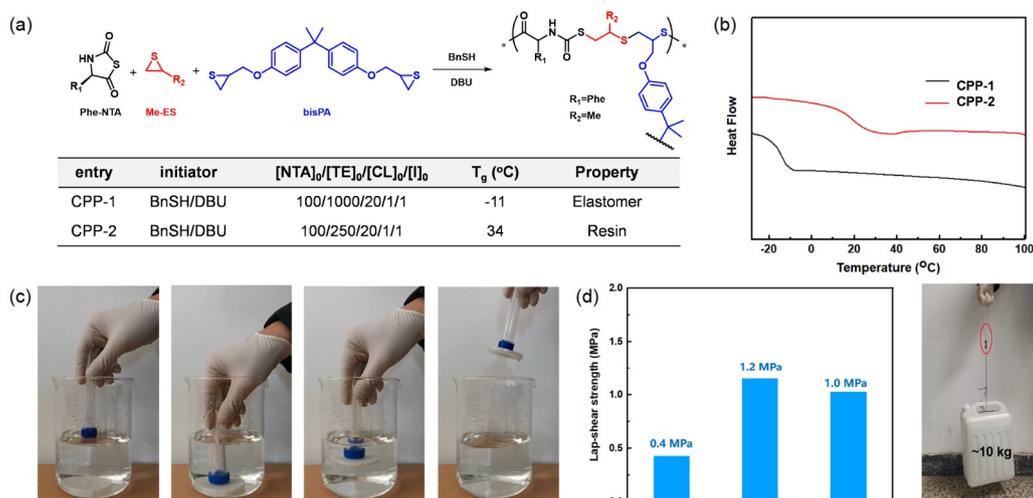


Figure 4 (a) The ROCOP results of Phe-NTA, Me-ES, and bisPA yielding two crosslinked polymers, CPP-1 and CPP-2. (b) The DSC curves of CPP-1 and CPP-2. (c) Photographs of the underwater adhesion performance of CPP-1. (d) The lap shear strength of CPP-2 and a photograph showing the loading capacity of CPP-2 adhesive (color online).

7–12, Table 1). We also attempted to replace Me-ES with 1,1-dimethyl episulfide (Gem-ES) for the ROCOP with Phe-NTA. However, the full conversion of the monomer required ~120 h due to the lower reactivity of Gem-ES as compared with Me-ES, and the resulting copolymers still displayed low M_n below ~5,000 g/mol (entries 13 and 14, Table 1). We speculated that the low M_n was due to the highly dynamic P(TU-*alt*-TE) backbone, which may give rise to extensive chain transfer and chain backbiting side reactions during the ROCOP process.

To overcome the limitations of the low M_n of the P(TU-*alt*-TE), we synthesized a bifunctional monomer, denoted as bisPA, as a crosslinker. We then prepared dynamic P(TU-*alt*-TE) networks (Figure 4a) through the ROCOP of NTA, ES, and bisPA at two different feeding ratios. By adjusting the feeding ratio of Phe-NTA, the T_g of the polymer network ranged from approximately -11 to 34 °C, and the resulting crosslinked P(TU-*alt*-TE) (CPP) exhibited elastomer/resin-like properties (Figure 4b). Both materials exhibited certain adhesion properties. As shown in Figure 4c, CPP-1 maintained good adhesion on a glass substrate even after being submerged in water for 24 h. For CPP-2, the adhesion performance was improved significantly at temperatures above its T_g (~34 °C), making it suitable as a hot-melt adhesive. For instance, after hot-compression treatment, CPP-2 was found to tightly bond aluminum substrates together even after being immersed in water for 24 h (Figure 4d). CPP-2 also showed a significant improvement in adhesion strength compared with CPP-1, reaching a lap shear strength of ~1.2 MPa between two aluminum surfaces. As a control, we found that the bisPA-crosslinked pES network did not show any adhesive property (data not shown). Together, we attributed the adhesive properties of the PTU networks mainly to the hydrogen bond interactions between the thiourethane

bonds in the polymer network and the hydroxyl groups on the substrate surface.

3 Conclusions

In summary, we successfully achieved the alternating ROCOP of NTAs and ESs, which offered an efficient approach for synthesizing unprecedented P(TU-*alt*-TE) copolymers. The alternating and regioselective structure of the resulting P(TU-*alt*-TE)s was confirmed using experimental techniques such as NMR and MALDI mass spectrometry. Furthermore, the mechanism behind the formation of alternating sequences was revealed through DFT calculations. Although the MW control of the ROCOP system was unsatisfactory, we were able to obtain a range of dynamic PTU networks by using bifunctional monomers as crosslinkers. Due to the abundant amide bonds in their backbone, these networks exhibited good adhesive properties and potential applications as hot-melt adhesives.

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Conflict of interest The authors declare no conflict of interest.

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