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Facile Synthesis of Polyisothioureas *via* Alternating Copolymerization of Aziridines and Isothiocayanates

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Electronic Supplementary Information

Abstract Isothiourea is an important class of sulfur-containing molecules showing unique catalytic and biological activities. As such, polyisothiourea is envisioned to be an interesting type of polymer that potentially exhibits a number of interesting properties. However, there is no access to synthesizing well-defined polyisothiourea, and currently isothiourea-containing polymers are mainly prepared by immobilizing onto other polymer's side chain. Herein, we report the first facile synthesis of polyisothioureas *via* alternating copolymerization of aziridines and isothiocayanates. Mediated by the catalytic system of phosphazene superbases/alcohol, a broad scope of aziridines and isothiocayanates could be transformed into polyisothioureas with adjustable substitutions (11 examples). The structures of obtained polyisothioureas were fully characterized with ^{1}H-NMR, ^{13}C-NMR, and ^{1}H-^{13}C HMBC NMR. Moreover, the polyisothioureas show tunable thermal properties depending on substitutions on the isothiourea linkages. The novel structure of these polyisothioureas will enable a powerful platform for the discovery of next-generation functional plastics.

Keywords Polyisothioureas; Alternative copolymer; Aziridines; Isothiocayanates

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INTRODUCTION

Sulfur-containing polymers process outstanding characteristics including optical,[1,2] mechanical[3] and electric[4,5] properties, heavy-metal recognition ability,[6,7] and recyclability.[8,9] Therefore, the development of new sulfur-containing polymers continues to be an important frontier in the field of polymer chemistry. Notable examples of such polymers include polythioethers,[10] polythioesters,[2] polythiourethanes,[11] polythiocarbonates,[12,13] and polythioureas.[6,14] Isothiourea, a tautomer of thiourea, is a versatile structural motif showing a multitude of catalytic,[15] agrochemical and biological potencies.[16–18] Recently, polymer-supported isothioureas have also attracted considerable attention as immobilized catalysts for diverse chemical transformations.[19–21] Specifically, the polymers featuring isothiourea moiety showed good selectivity and reactivity on cycloaddition ([8+2] and [4+2] annulation reactions) and alcohol's kinetic resolution within broad substrate scope. And notably, higher stereoselectivity was discovered for the isothiourea-loaded polymer compared with its homogeneous counterpart.[20] In light of the success of discrete and polymer-bounded isothioureas, polyisothiourea, as a new class of sulfur-containing polymers, is envisaged to potentially exhibit a number of interesting properties. However, attempts at preparing well-defined polyisothioureas have been unsuccessful, as reliable synthetic approaches are yet to be developed, let alone the adjustment of polymer microstructure. To our knowledge, the only traceable demonstration of polyisothiourea was published in the 1960s from 1,5 polymerization of a thiocarbamylaziridine.[22] However, the obtained polymer was poorly defined due to limited solubility in common solvents, and only illuminated as a polymer containing isothiourea linkage by infrared spectra.

Alternating ring-opening copolymerization (ROCOP) is a chain-growth approach with excellent control over sequence, molecular weight and dispersity.[23] To date, ROCOP is amenable to a variety of heterocycles and heteroallenes. From these relatively simple comonomers, ROCOP permits the formation of many completely new polymer microstructures. Recently, iso(thio)cyanate has attracted considerable attention as a new class of ROCOP comonomers to form poly(thio)urethanes. In 2020, Adriaenssens and coworkers reported the seminal discovery of using isocyanates and epoxides as ROCOP comonomers to synthesize novel polyurethanes with fully substituted carbamyl nitrogen atoms.[24] Subsequent efforts by Feng,[25,26] our group,[27] Lu,[28] and

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others[29−32] have resulted in controlled ROCOP of diverse iso(thio)cyanate and epoxide/episulfide. While the alternating copolymerization with iso(thio)cyanate have received significant attention, challenging scope of heterocycle monomer constrains accessible polymer structures and properties. To open up the synthetic route to polyisothiourea, our attention has been drawn towards aziridines, who are versatile intermediates for the synthesis of many important compounds.[33] In light of the structural similarity between aziridines and epoxides and our prior copolymerization results with isocyanates,[34] we envisioned the alternating copolymerization of aziridines and isothiocayanates would be a viable strategy to precisely synthesize polyisothiourea that is otherwise inaccessible.

Herein, we report the first facile synthesis of polyisoureas *via* alternating ROCOP of aziridines and isothiocayanates (Scheme 1). Under the catalytic system of phosphazene superbases/BDM, isothiocayanates and aziridines were successfully coupled to form polyisothioureas, where the reactivity and polymer selectivity varied among monomer with different substitutions. The polyisothiourea structures were validated by ^{1}H-NMR, ^{13}C-NMR and ^{1}H-^{13}C HMBC NMR, meanwhile, their molecular wight and dispersity were demonstrated by gel permeation chromatography (GPC). A possible mechanism of alternatively incorporated isothiocayanates and aziridines was further proposed.

EXPERIMENTAL

General

All experiments were carried out in a dry argon atmosphere using standard Schlenk techniques or in a glovebox unless stated. 1-benzyl aziridine (BnAz), 1-(4-fluorobenzyl)-aziridine (FBnAz), *n*-butyl aziridine (*n*BuAz) were synthesized according to literature.[11,34−36] Phenyl isothiocyanate (PITC), 4-fluorophenyl isothiocyanate (FPIC), *p*-tolyl isothiocyanate (PTITC), *o*-tolyl isothiocyanate (OTITC) were purchased from Aladdin Chemical and distilled before use. ^{t}Bu-P$_1$, ^{t}Bu-P$_2$, ^{t}Bu-P$_4$, MTBD, DBU and benzenedimethanol (BDM) were purchased from Sigma-Aldrich and directly used.

Measurements

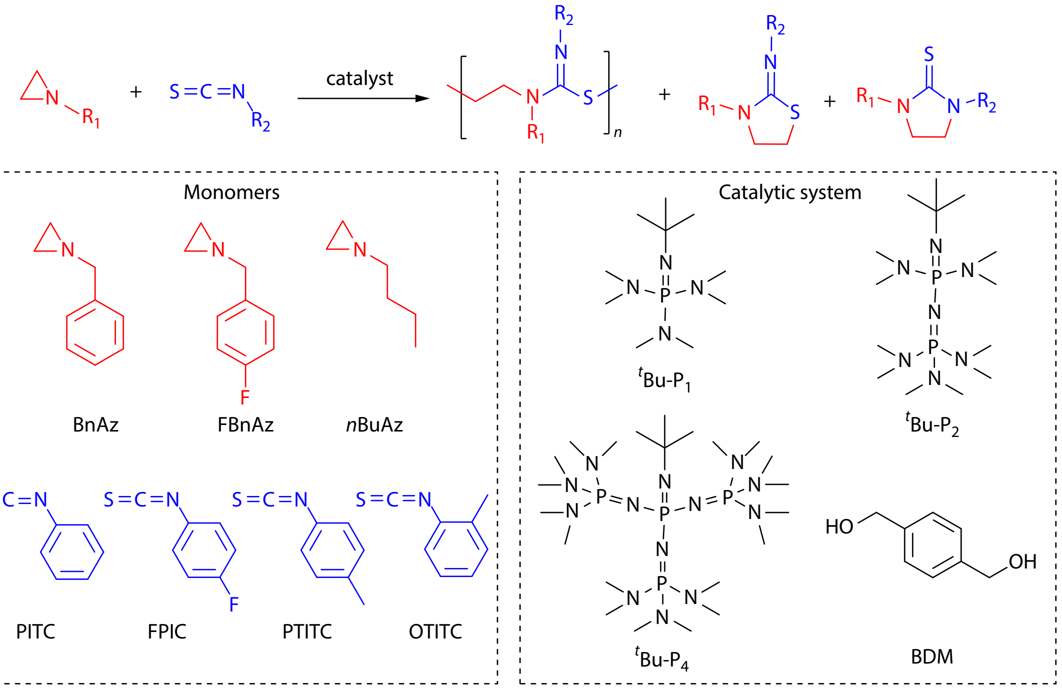
NMR spectra were recorded on Bruker AV 300MHz and Bruker AV 500MHz in $CDCl_3$ at 25 °C. Chemical shifts were given in parts per million from tetramethylsilane. Gel permeation chromatography (GPC) measurements were conducted with a Waters 515 GPC with DMF/LiBr (0.5 mL/min) as the eluent (Waters 515 HPLC Pump, Waters 2414 Refractive Index Detector, Waters Styragel GUARD COLUMN+HT4 DMF, poly(methyl methacrylate) (M_n=875−332800 kg·mol^{-1}) standards, and 50 °C). *In situ* ATR-IR reaction was monitored using a Mettler-Toledo ReactIR 15 spectrometer equipped with a MCT detector and a silver halide DiComp probe.

General Polymerization Procedure

In a typical polymerization experiment, isothiocayanates were loaded in a flame-dried vial containing a magnetic bar, and catalytic system in desired ratios was added and dissolved in isothiocayanates. The vial was sealed under argon, and placed in an oil bath thermostated, followed by injection with desired amount of aziridine monomer. After a certain reaction time, minimal amount of sample was withdrawn for ^{1}H-NMR analysis. The polymers were isolated by precipitating into ethanol. The precipitate was collected and dried under vacuum at 40 °C overnight.

RESULTS AND DISCUSSION

Initially, the copolymerization of aziridines and isothiocayanates was systematically explored with phosphazene superbases/



Scheme 1 Alternating copolymerization of isothiocayanates and aziridines under phosphazene superbases/BDM.

Table 1 Data for the copolymerization of aziridines with isothiocayanates. [a]

Entry	Aziridine	Isothiocayanate	Catalyst	Time (h)	Conv. [b] (%)	Poly:cyc [b]	$M_{n,GPC}$ [c] ($kg\cdot mol^{-1}$)	$Đ$ [c]
1	BnAz	PITC	^{t}Bu-P$_1$/BDM	0.2	83	80:20	12.6	1.23
2	BnAz	PITC	–	3	0	–	–	–
3 [d]	BnAz	PITC	^{t}Bu-P$_2$/BDM	0.1	82	91:9	27.6	1.23
4	BnAz	PITC	MTBD/BDM	0.2	76	90:10	11.9	1.40
5	BnAz	PITC	DBU/BDM	0.4	68	88:12	10.2	1.34
6	BnAz	FPIC	^{t}Bu-P$_1$/BDM	0.5	94	55:45	11.8	1.40
7	BnAz	PTITC	^{t}Bu-P$_4$/BDM	3	91	53:47	8.0	1.34
8	BnAz	OTITC	^{t}Bu-P$_4$/BDM	3	86	80:20	13.1	1.29
9	FBnAz	PITC	^{t}Bu-P$_1$/BDM	0.2	74	83:17	7.8	1.21
10	FBnAz	FPIC	^{t}Bu-P$_1$/BDM	0.5	73	22:78	11.8	1.26
11	FBnAz	PTITC	^{t}Bu-P$_4$/BDM	3	96	66:34	5.5	1.21
12	FBnAz	OTITC	^{t}Bu-P$_4$/BDM	3	71	97:3	38.5	1.42
13	nBuAz	PITC	^{t}Bu-P$_2$/BDM	4	99	94:6	1.5	1.18
14	nBuAz	FPIC	^{t}Bu-P$_2$/BDM	4	99	98:2	2.4	1.57
15	nBuAz	PTITC	^{t}Bu-P$_2$/BDM	4	– [e]	– [e]	– [e]	– [e]
16	nBuAz	OTITC	^{t}Bu-P$_2$/BDM	4	99	96:4	0.9	1.03

[a] Polymerization conditions: 0.3 g of aziridine, [aziridine]:[isocyanate]:[catalyst] = 250:250:1, T_{rxn} = 25 °C.; [b] Conv. (conversion of aziridine monomer) and poly:cyc (selectivity of polymer over cyclic byproduct): determined from the ^{1}H-NMR spectra of crude mixtures; [c] Obtained by GPC analysis (DMF) and calibrated against the poly(methyl methacrylate) standard; [d] [aziridine]:[isocyanate]:[catalyst] = 500:500:1; [e] Result in insoluble solid that cannot be characterized.

benzenedimethanol (BDM), a successful catalytic system for a variety of ROCOP comonomers.[23,37] The results are summarized in Table 1. In the presence of 0.4 mol% ^{t}Bu-P$_1$/BDM, the neat system of stoichiometric 1-benzyl aziridine (BnAz) and phenyl isothiocyanate (PITC) was observed to gradually solidify in 0.2 h.

The same comonomers were also mixed in the absence of catalysts, and no reaction occurred after 3 h (Table 1, entry 2). Upon purification by precipitating into ethanol, the polymer could be obtained as a white solid, which had a molecular weight of 12.6 $kg\cdot mol^{-1}$ and relatively narrow $Đ$ (1.23) (Table 1, entry 1). The microstructure of obtained polymer was first identified by ^{1}H- and ^{13}C-NMR (Fig. 1). As shown in the ^{1}H-NMR spectrum (Fig. 1a), the characteristic signals of the phenylmethyl and methylene protons adjacent to (iso)thiocarbamide appeared at 4.5 ppm (a), 3.3 ppm (b) and 2.5 ppm (c), rationalizing the (iso)thiourea linkage. In the ^{13}C-NMR spectrum (Fig. 1b), the signal of isothiocarbamide linkages appeared at 152 ppm, providing strong evidence to rule out the existence of thiourea linkage whose signal appearing at ~180 ppm.[6,14] Thus, the formation of polyisothiourea from alternating copolymerization of BnAz and PITC was confirmed. Moreover, the structure was also validated by ^{1}H-^{13}C HMBC NMR (Fig. S1 in ESI) and FTIR (Fig. S2 in ESI). After clearly analyzing the NMR spectra of produced polyisothiourea, we were able to calculate the monomer conversion and selectivity of polymer over cyclic (iso)thiourea byproducts (Fig. S3 in ESI). For the copolymerization of BnAz and PITC (Table 1, entry 1), after 0.2 h, 83% of monomer was

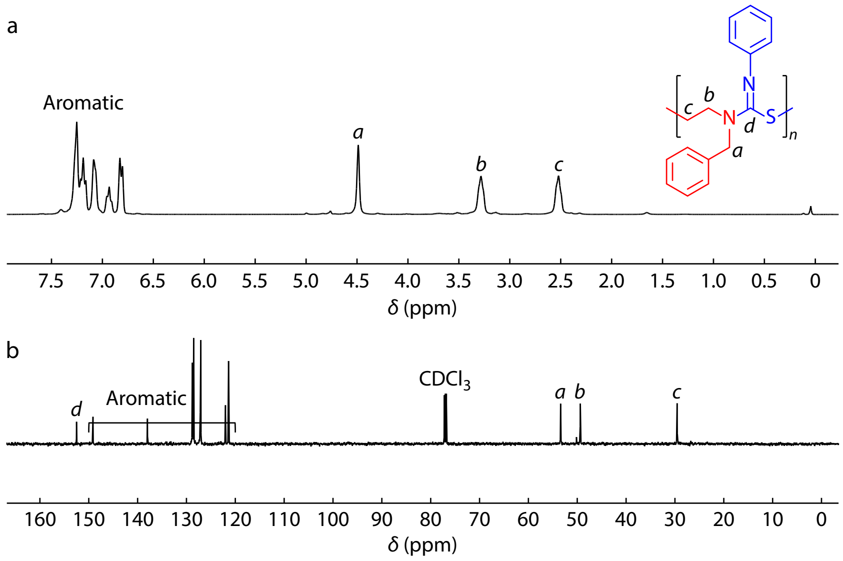


Fig. 1 (a) ^{1}H-NMR spectrum and (b) ^{13}C-NMR spectrum for the polymer synthesized from BnAz with PITC.

converted with 80% selectivity for polymer formation over cyclic side products. The copolymerization process was also monitored by *in situ* attenuated total reflection-infrared (ATR-IR) spectroscopy (Fig. 2). A gradual increase ofintensity of (N/S)C=N group's band at 1592 cm^{-1} was observed, mirroring the previously observed continuous formation of isothiourea linkage during polymerization. Under low feeding of catalytic system, higher molecular weight (13.1 $kg \cdot mol^{-1}$) was achieved (Table 1, entry 3). Generally, the organic bases with higher basicity were discovered to show enhanced efficiency and selectivity for the copolymerization of the same aziridine/isothiocyanate comonomer pairs. And other organic bases with weaker basicity (MTBD, DBU) were also available for mediating this copolymerization (Table 1, entries 4 and 5), where a slightly increase of $Đ$ to 1.34–1.40 was observed.

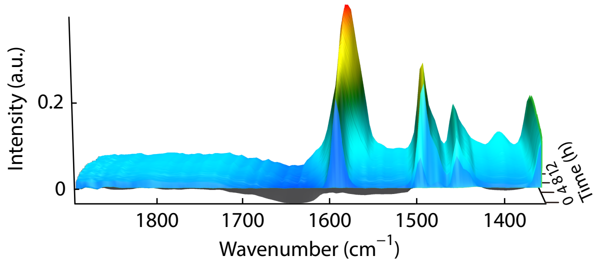


Fig. 2 *In situ* FTIR spectroscopy measuring the $\nu_{C=N}$ band area (1592 cm^{-1}) during copolymerization of BnAz and PITC mediated by ^{t}Bu-P_1/BDM ([BnAz]=1 mol/L in THF).

Next, the copolymerization of other comonomer pairs except for BnAz and PITC was investigated. ^{t}Bu-P_1 could also efficiently mediate the copolymerization of BnAz and 4-fluorophenyl isothiocyanate (FPIC) to produce polyisothiourea with similar molecular weight (11.8 $kg \cdot mol^{-1}$) and dispersity ($Đ$=1.40), albeit with a decreased polymer selectivity of 55% (Table 1, entry 6). For isothiocyanateswith methyl substitution on the benzene ring, *i.e.*, *p*-tolyl isothiocyanate (PTITC) and *o*-tolyl isothiocyanate (OTITC), a more reactive phosphazene catalyst (^{t}Bu-P_4) and longer reaction time (3 h) are required (Table 1, entries 7 and 8). Moreover, higher polymer selectivity of BnAz/OTITC during polymerization was observed (80%) compared to that of BnAz/PTITC (53%), while the molecular weight of obtained polymer for BnAz/OTITC (13.1 $kg \cdot mol^{-1}$) is also higher than BnAz/PTITC (8.9 $kg \cdot mol^{-1}$). And the dispersity retained relatively narrow ($Đ$~1.30). When FBnAz was used as the aziridine comonomer instead of BnAz, the copolymerization follows essentially the same trend in terms of reactivity and selectivity (Table 1, entries 9–12). Similarly, ^{t}Bu-P_1/BDM could mediate the copolymerization of FBnAz and PITC or FITC, while ^{t}Bu-P_4/BDM and longer time (3 h) were required for that of FBnAz and PTITC or OTITC. Of note, high polymer selectivity (97%) and molecular weight (38.5 $kg \cdot mol^{-1}$), as well as relatively wide $Đ$ (1.42) from the copolymerization FBnAz/OTITC were observed (Table 1, entry 12), while the other copolymerizations with FBnAz resulted in lower polymer selectivity (22%–83%) and molecular weights (7.8–11.8 $kg \cdot mol^{-1}$) as well as narrow $Đ$s (1.21–1.26) (Table 1, entries 9–11). At last, we studied the copolymerizations of nBuAz and isothiocyanates (Table 1, entries 13–16). We discovered that a modest phosphazene superbase system of ^{t}Bu-P_2/BDM is the most suitable for these copolymerizations, in which quantitative conversion and high polymer selectivity (~96%) could be facilitated after 4 h. However, while copolymer from *n*BuAz and PITC/FIPC/OTITC could be obtained, the molecular weights were relatively low (0.9–2.4 $kg \cdot mol^{-1}$) (Table 1, entries 13–15). The ^{1}H- and ^{13}C-NMR spectra and the GPC traces of representative copolymers synthesized from aziridines and isothiocayanates are shown in Figs. S4–S23 (in ESI) and Fig. 3, indicating the production of polyisothioureas with a narrow monomodal chromatogram.

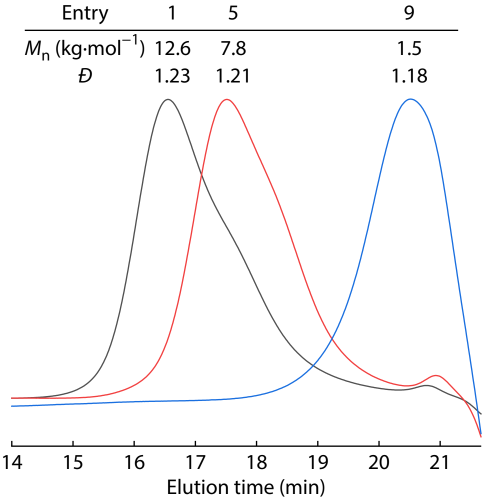
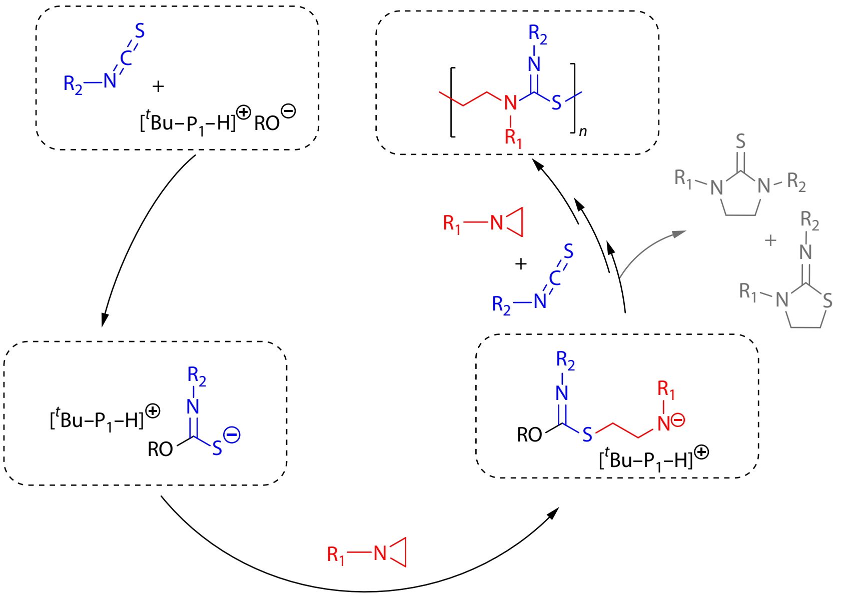


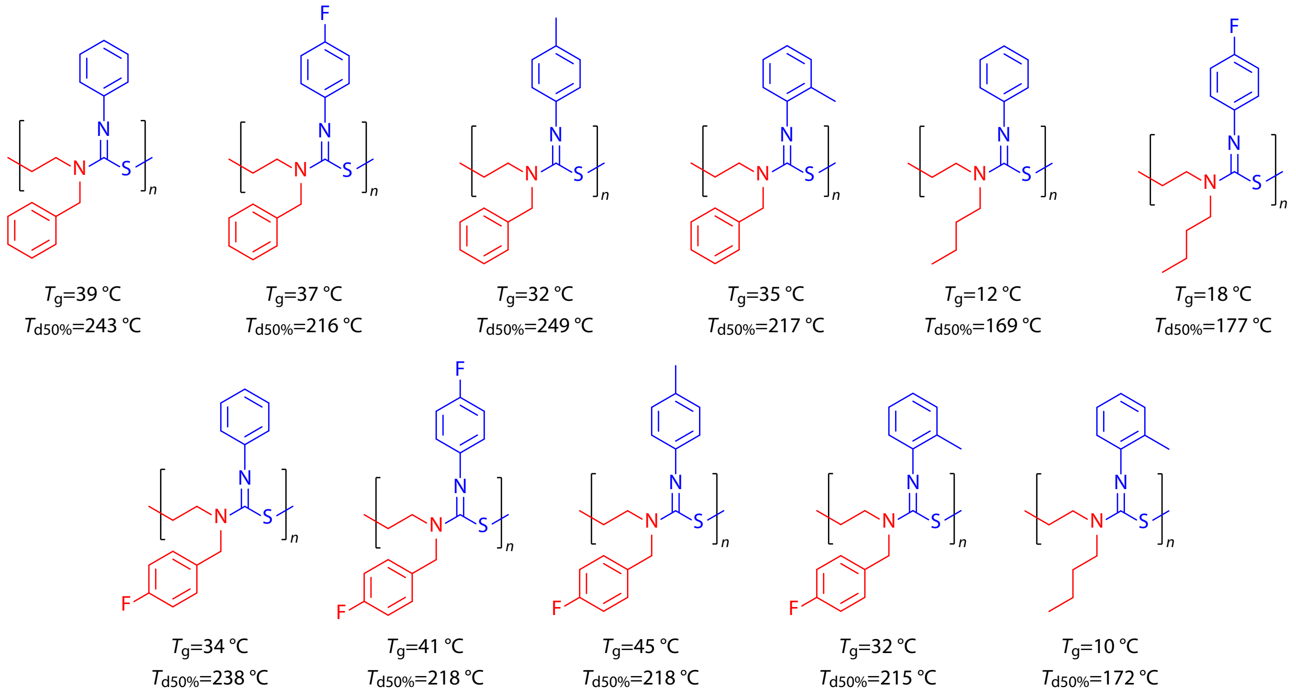
Fig. 3 GPC traces of representative copolymers synthesized from aziridines and isothiocayanates in Table 1.

Based on the above experimental results, we proposed a possible mechanism for the alternating copolymerization of aziridines and isothiocayanates (Scheme 2). First, the catalyst of phosphazene superbase like ^{t}Bu-P_1 deprotonates alcohols to form oxyanions, and subsequently attacks isothiocayanates to form —OC(=N)S— thioanions.[26] Because of the low preference of isothiocayanates to homo-polymerize the active species then tends to ring-open aziridines to form nitrogen anion. Thereafter, isothiocayanates and aziridines are alternatingly inserted to proceed the copolymerization, eventually forming polyisourea structure. During copolymerization, the inevitable backbiting reaction also results in the side product of cyclic (iso)thioureas.

At last, we studied the thermal properties of obtained polyisothioureas by differential scanning calorimetry (DSC, Figs. S24–S34 in ESI) and thermogravimetric analysis (TGA, Figs. S35–S45 in ESI). The data are summarized in Fig. 4, the polyisothioureas generally exhibit a T_g of 32–45 °C, while the ones with alkyl substitution have a lower T_g of 10–18 °C. Meanwhile, the polyisothioureas derived from *n*BuAz would decompose at a lower temperature with $T_{d50\%}$ of *ca.* 170 °C. And the highest $T_{d50\%}$ (243–249 °C) were observed for the polyisothioureas synthesized with BnAz and PITC/PTITC. We further studied the product from thermal decomposition through NMR (Fig. S46 in ESI). Interestingly, the copolymer synthesized from BnAz with PITC underwent quantitive thermal depolymerization under 200 °C to form cyclic isothiourea and thiourea, highlighting the recyclability of polyisothioureas.



Scheme 2 Proposed mechanism of ROCOP of aziridines and isothiocayanates.



T_g=39 °C $T_{d50\%}$=243 °C

T_g=37 °C $T_{d50\%}$=216 °C

T_g=32 °C $T_{d50\%}$=249 °C

T_g=35 °C $T_{d50\%}$=217 °C

T_g=12 °C $T_{d50\%}$=169 °C

T_g=18 °C $T_{d50\%}$=177 °C

T_g=34 °C $T_{d50\%}$=238 °C

T_g=41 °C $T_{d50\%}$=218 °C

T_g=45 °C $T_{d50\%}$=218 °C

T_g=32 °C $T_{d50\%}$=215 °C

T_g=10 °C $T_{d50\%}$=172 °C

Fig. 4 Thermal properties (observed T_g and $T_{d50\%}$ values) of obtained polyisothioureas.

CONCLUSIONS

In summary, we report the first synthesis of polyisothioureas *via* alternating ROCOP of aziridines and isothiocayanates using phosphazene superbases/BDM. Enabled by the good selectivity of the catalytic system, 11 examples of well-defined polyisothioureas were produced, and their structures were verified with NMR measurements. The substitutions on aziridine and isothiocayanate comomers were discovered to dramatically influence the reactivity, selectivity and molecular weight of the obtained polymers. Moreover, the formed polyisothioureas display adjustable thermal properties. Study of the catalytic and biological function of these polymers is ongoing in our laboratory.

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/s10118-023-3048-6.

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