

RESEARCH ARTICLE

Polyurethanes by ring-opening polymerization initiated from alcohol moiety-tethering acylazide

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Abstract

An orthogonal agent having both alcohol and acylazide groups was used to construct novel polyurethanes by a simple synthetic process. Ring-opening polymerization (ROP) of δ -valerolactone from the orthogonal agent afforded a crystalline polymer having acylazide initiation end, while that of δ -decanolactone resulted in an amorphous polymer. Since acylazide groups undergo thermally induced Curtius rearrangements to yield isocyanate groups, simple heating of above polymers gave macromonomers having both an isocyanate initiation end and an alcohol termination end, which afforded corresponding polyurethane by self-polyaddition in a bulk condition without any additives. Meanwhile, kinetic analysis of the Curtius rearrangement revealed that a quantitative conversion was reached within a short reaction time, for example at 110°C for 30 min, or at 100°C for 1 h. Moreover, obtained polyurethane species showed unique self-immolative type thermal degradation behavior. Considering the above, this orthogonal agent turned out to be useful to construct various polyurethane structures by a facile synthetic process, which would contribute to precise polymer synthesis and sequence defined polymer synthesis.

KEYWORDS

Curtius rearrangement, orthogonal agent, polyurethane, precise polymer synthesis, ring-opening polymerization, self-immolative polymer

1 | INTRODUCTION

Precise polymer synthesis is important, simply because the primary polymer structure defines most of its properties.¹ In general, precise polymer synthesis of chain polymerization has been more intensively studied than that on step-growth polymerization, probably because of different mechanism of the latter making it more difficult to address. One of the most popular polymer classes

synthesized by step-growth polymerization is polyurethane, which is typically synthesized by polyaddition reaction between di-isocyanate and diol monomers.² In general, such polyurethane synthesis does not focus on building elaborate polymer repeating pattern, which is commonly reached in chain polymerization system, opening the avenue to block or alternating copolymer structures. To address a precise polymer synthesis for polyurethanes, multiple approaches have been reported, such as the sequential

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monomer addition or polymerization of cyclic monomer species.³ However, these methods often face inevitable limitations by taxing multistep synthesis, which also results in the achievement of precise synthesis only on an oligomer level. Therefore, new precise synthesis on polyurethanes that is based on an easy synthetic process is highly desired. Moreover, such a precise synthetic method would contribute to implement elaborate molecular design, such as supramolecular architecture construction, stimuli-responsive materials, battery materials, and so on,⁴ in addition to the studies focusing on polyurethane framework itself, supporting its importance.

In this regard, Akae, Takata, and co-workers reported to use an orthogonal agent featuring both alcohol and acylazide moieties for syntheses of various polyurethane architectures (Figure 1A).⁵ Since the acylazide group undergoes a heat-induced Curtius rearrangement to transform into an isocyanate group quantitatively, such orthogonal agents can be used as an AB-type monomer for the polyurethane synthesis. As reported, the hydroxyl group on this agent can initiate a ring-opening polymerization (ROP) of δ -valerolactone (VL), resulting in a crystalline polyester exhibiting an isocyanate initiation end, which was also used to synthesize polyurethane-polyester block copolymer in a facile manner. On the other hand, the polymer having an acylazide initiation end and a hydroxyl termination end would work as a macromonomer for polyurethane synthesis, although this issue has not been studied yet. Furthermore, other cyclic monomers than δ -valerolactone, which can undergo a ring-opening polymerization initiated from the hydroxyl group, would also afford corresponding polymer framework, providing the applicability of this protocol can be further extended. Meanwhile, this orthogonal framework

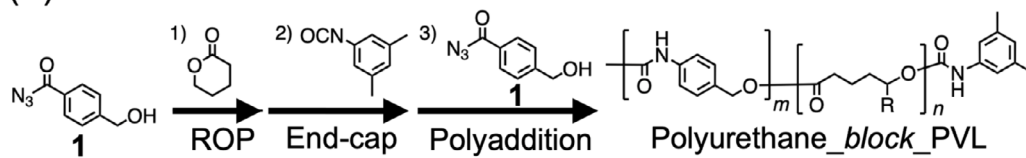
can be easily addressed by the commercial products, suggesting the further development along this molecular design could expand its versatility on the precise polymer synthesis on polyurethane framework by facile synthesis, which is difficult to be addressed by other synthetic methods. Considering the above, in this work, we studied novel polyurethane framework construction based on the macromonomer species obtained by ROP from the orthogonal agent, to expand the versatility of this synthetic method (Figure 1B). In addition to VL, which was previously reported, δ -decanolactone (DL) was applied in this framework for the first time to afford amorphous polyesters featuring an isocyanate termination end. Interestingly, the obtained macromonomers turned out to polymerize effectively by a simple heating in bulk without any additives to afford corresponding polyurethane framework. Synthetic details including the kinetic analysis of Curtius rearrangement are demonstrated in the following.

2 | RESULTS AND DISCUSSION

As previously reported, an orthogonal agent 1 (4-hydroxymethyl benzoylazide) was synthesized from the commercial carboxylic acid by the reaction with diphenyl phosphoryl azide (DPPA).^{5,6} Although the self-polyaddition of 1 to P1 was demonstrated already,⁵ the kinetics of Curtius rearrangement and its polymerization behavior have not been investigated in detail, which is addressed in the following.

First of all, 1 was heated at 110°C for 30 min in bulk condition without any additives to check if the intermediated product 1_NCO could be observed (Scheme 1A).

(A) Previous work



(B) This work

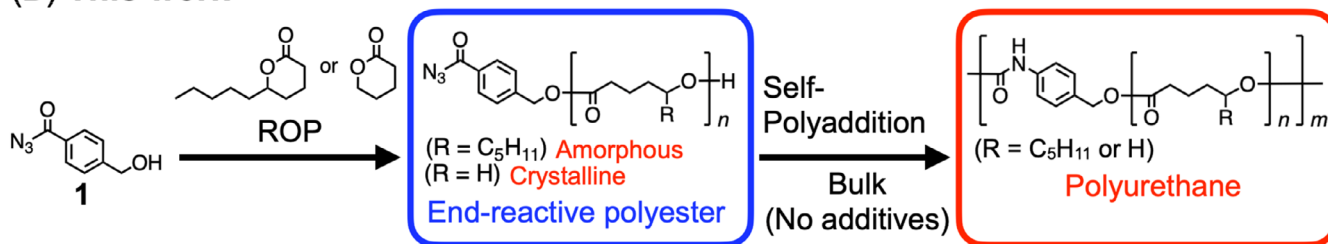


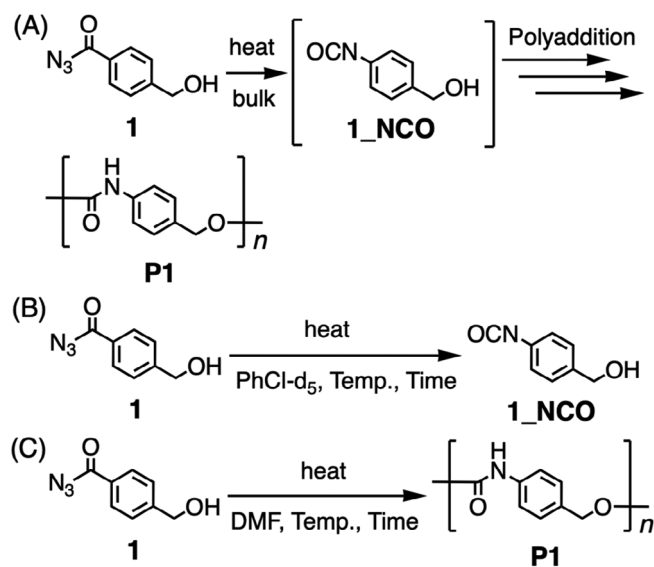
FIGURE 1 Schematic illustration of polyurethane framework construction via the end-reactive polyester synthesized by ROP initiated from the hydroxyl group of 1; (A) previous work⁵ and (B) this work.

However, the ^1H nuclear magnetic resonance (NMR) spectrum of the heated sample only showed signals from P1, while the size-exclusion chromatography (SEC) result showed the existence of polymer species although the signal had multimodal tailing pattern on the low molecular weight region, suggesting that the polymerization occurred under this reaction condition. Though the reaction between isocyanate and hydroxyl group often requires some catalyst to reach high conversion,^{5,6} the reaction proceeded well in this condition probably owing to high temperature (110°C) and high concentration (bulk). Therefore, to observe the isocyanate intermediate 1_NCO, 1 was heated at low concentration to prevent self-polyaddition. Also, since 1_NCO underwent the self-polyaddition soon at its favorable condition, the kinetics of the Curtius rearrangement of 1 was investigated under diluted conditions.

Kinetic and thermodynamic analyses of the Curtius rearrangement was carried out as followings.⁷ 1 was dissolved in PhCl-d_5 as an inert solvent, which has an appropriate boiling point, at 0.10 M concentration and heated at 100°C (Scheme 1B). After 5, 10, and 15 min, ^1H NMR measurements were conducted (Figure 2). Over the course of the heating time, the signals from 1 decreased and new signals from 1_NCO increased without an accompanying emergence of P1, clearly indicating the progress of Curtius rearrangement reaction.⁸ Soon after heating, the sample appeared as a homogeneous transparent solution, but when it was kept at room temperature overnight, a solid formed, which suggested the production of polyurethane species whose solubility in

PhCl-d_5 was not high. According to the integration of the distinctive ^1H NMR signals, a kinetic constant and half-life time of this reaction was calculated (the details of the kinetic analysis are described in ESI). In a similar manner, the same analyses were carried out at 110 and 90°C, respectively, and the calculated parameters are summarized in Table 1. From here, it was also calculated that the conversion reached over 99% at 110°C within 23 min, while at 100°C it took 54 min.⁸ Although this kinetic study is only accurate for the reaction in PhCl-d_5 at 0.10 M concentration, a similar kinetic behavior can be predicted under other similar reaction conditions, because the Curtius rearrangement reaction is a heat-induced intramolecular reaction. Therefore, heating at 110°C for 30 min, or at 100°C for 1 h, can be considered as a rough guideline to reach quantitative conversion of the Curtius rearrangement in other reaction condition. Moreover, these thermodynamic parameters will be useful to compare the reaction behavior with other orthogonal agents in the future.

Considering the results from the kinetic analysis, self-polyaddition of 1 was carried out via formation of 1_NCO by Curtius rearrangement under various reaction conditions (Scheme 1C). Namely, 1 was heated in DMF at 1.0 M concentration at least longer than 30 min at 110°C, or 1 h at 100°C, and afterwards the reaction mixture was kept at certain conditions depicted in Table 2 to investigate the further progress of the polymerization. Also, the effect of the addition of dibutyltin dilaurate (DBTDL) as catalyst, which is a typical catalyst of such polyurethane synthesis, was investigated.⁵ Each polymerization mixture was quenched by precipitating into MeOH, analyzed by SEC and ^1H NMR measurement, and the results are summarized in Table 2. In short, all conditions afforded



SCHEME 1 Heat-induced Curtius rearrangement of 1 (A) under bulk condition; (B) 0.10 M of PhCl-d_5 solution; and (C) 1.0 M of DMF solution.

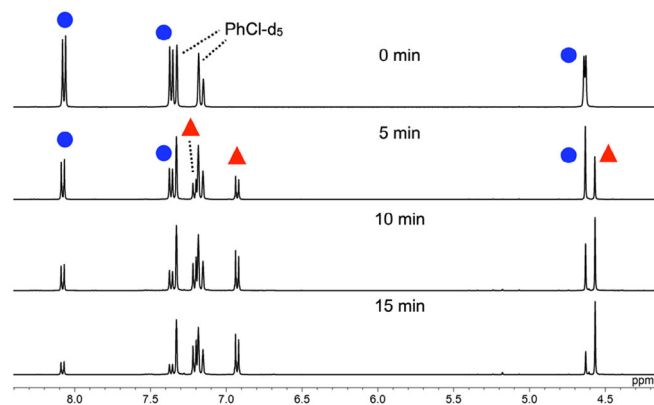


FIGURE 2 Time-dependent ^1H NMR spectral changes around the 8.0–4.5 ppm region (400 MHz, PhCl-d_5 , 298 K) during the Curtius rearrangement reaction of 1. The peaks are marked as 1 (●) and 1_NCO (▲).

TABLE 1 Kinetic and thermodynamic parameters on the Curtius rearrangement of 1 (Scheme 1B).

Temp. [°C]	Rate constant k [s ⁻¹]	Half-life τ [min]	Activation energy E [kJ mol ⁻¹]	Activation enthalpy ΔH^\ddagger [kJ mol ⁻¹]	Activation entropy ΔS^\ddagger [J mol ⁻¹ K ⁻¹]
90	5.8×10^{-4}	20	105	102	-26
100	1.5×10^{-3}	7.6			
110	3.6×10^{-3}	3.2			

[‡]Indicates the parameter relevant with activation status.

TABLE 2 Polymerization of 1 in DMF (Scheme 1C).

Entry	1st condition	2nd condition	Yield [%]	M_n [kDa] ^b	M_w [kDa] ^b	\bar{D}^b
1	110°C, 3 h	DBTDL, r. t., 24 h	74	13	18	1.5
2	DBTDL, 110°C, 3 h	- ^a	62	10	18	1.8
3	DBTDL, 110°C, 24 h	- ^a	27	13	35	2.6
4	100°C, 1 h	DBTDL, r. t., 24 h	71	11	18	1.6
5	DBTDL, 110°C, 30 min	- ^a	75	11	16	1.5
6	110°C, 30 min	DBTDL, r. t., 30 min	75	12	16	1.4
7	110°C, 30 min	- ^a	79	13	18	1.4
8	110°C, 15 min	- ^a	58	13	17	1.3
9	110°C, 1 h	DBTDL, r. t., 24 h	77	13	18	1.4

^aNot conducted.

^bCalculated by SEC (eluent; DMAc, flow rate; 0.5 mL/min, 50°C).

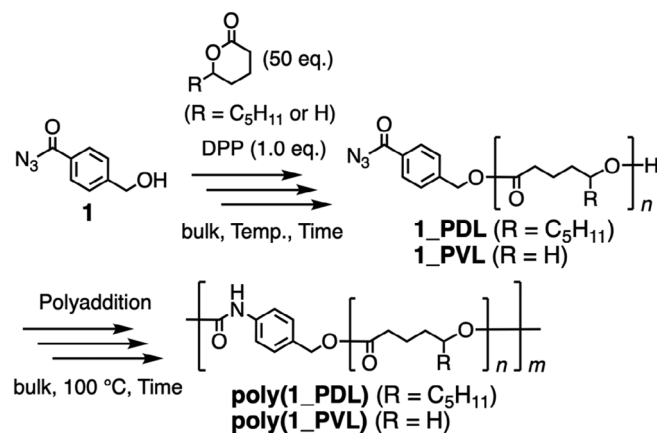
P1, but the yield and molecular weight changed depending on the reaction condition.

Here, when the reaction condition was changed in the middle of the polymerization process, it is written as 2nd condition in Table 2, while the initial condition is depicted as 1st condition. As a result, it turned out that the most part of the monomer conversion and the propagating process proceeded within 30 min at 110°C without any catalyst (Table 2, entry 7), and the further extension of the reaction time did not effectively increase the molecular weight of the polymer (Table 2, entries 1, 6, and 9), while long heating times at high temperature induced lower yields and high \bar{D} value (Table 2, entries 2 vs. 3). Since urethane bonds can reversibly be cleaved at high temperature and regenerated isocyanate group, this would enable irreversible side reaction, such as the formation of biuret species, and so on,² thus reducing the yield of polyurethane when heating the reaction mixture for a long time. Notably, the addition of DBTDL did not effectively increase the molecular weight in this polymerization system (Table 2, entries 5 vs. 7), which afforded already high molecular weight without any catalyst. Probably in other reaction condition, such as in other solvent or at lower concentration, the existence of the catalyst might contribute to promote the polymerization progress, but it was not necessary under the current polymerization condition. Since DBTDL could also catalyze side reactions, such as the urethane bond cleavage or

biuret species formation, the catalyst addition does not directly result in the promotion of the polymerization. Heating at 100°C was also conducted (Table 2, entry 4), but no significant difference was observed compared with 110°C. Since the Curtius rearrangement proceeds faster at 110°C than at 100°C without accompanying any undesired issues, 110°C could be a preferable temperature herein. Meanwhile, the reaction was stopped after heating at 110°C for 15 min (Table 2, entry 8). Based on the kinetic data, the conversion of the Curtius rearrangement in 0.10 M PhCl-d₅ solution after heating at 110°C for 15 min reaches 96%,⁸ although this value is not exactly accurate under the polymerization condition (1.0 M DMF solution). There, the molecular weight of the polymer reached already as high value as other entries ($M_n = 13$ kDa), and simply the yield decreased (58% on entry 8 vs. 79% on entry 7). Therefore, it was speculated that the polymerization itself proceeds quite fast compared with the rate of the Curtius rearrangement, and polymer species reached a certain degree of polymerization soon where further increase becomes slower. Interestingly, such polymerization behavior could resemble to that of chain polymerization, such as free radical polymerization, where the generation of active species induces the fast polymerization progress and quenched soon after the termination. Although further detailed analysis is difficult owing to the low solubility of P1 in PhCl-d₅ and beyond the scope of this work, it could be

considered that the combination of the transformation reaction from the monomer precursor to the actual monomer species and its polyaddition reaction would provide a unique polymerization system. Anyhow, it turned out that M_n of P1 reached over 10 kDa soon and further increase was not easy to achieve. Since the solubility of P1 in general organic solvent was not so high, it might cause the difficulty to reach further increase of the molecular weight, meaning the modification of the monomer structure to increase the solubility of the resulting polymer would contribute to synthesize polyurethane species having higher molecular weight. Meanwhile, such a low solubility of P1 would be beneficial to build a precipitation polymerization system, suggesting an expected application along this line.

Next, ROP of VL and DL were carried out from the hydroxyl group on 1 with diphenylphosphate (DPP) catalyst in a bulk condition to synthesize 1_PVL and 1_PDL (Scheme 2, Table 3). As previously reported, the polymerization of VL completed within a short reaction time at r. t., and corresponding polymer 1_PVL was synthesized in a good yield by facile process.⁵ Meanwhile, according to the previous study,⁹ the polymerization of DL required much longer reaction time than that of VL at 40°C. Therefore, the polymerization of DL was carried out for 16 and 72 h, which was much longer than that of VL (3 h). In both reaction condition, the corresponding



SCHEME 2 ROP of lactone monomers and successive polyaddition.

TABLE 3 Reaction condition of ROP by Scheme 2.

Polymer	Monomer	Temp. [°C]	Time [h]	Yield [%]	$M_{n,NMR}$ [kDa]	M_n [kDa] ^a	M_w [kDa] ^a	\bar{D}^a
1_PVL	VL	r. t.	3	88	5.1	6.2	7.2	1.2
1_PDL_4.8	DL	40	16	38	4.8	6.5	7.3	1.1
1_PDL_8.0	DL	40	72	53	8.0	9.7	12	1.2

^aCalculated by SEC (eluent; THF, flow rate; 1.0 mL/min, 25°C).

polymer 1_PDL was successfully synthesized and detected by ¹H NMR and SEC measurement (Figures 3 and 4). However, the yield after 16 h reaction time (38%) was lower than that for 72 h (53%), which was consistent with the previous study,⁹ meaning further prolonging the reaction time is required to reach high conversion of DL monomer. Molecular weight $M_{n,NMR}$ of each polymer was calculated by the integration of the initiation end and polyester repeating unit, and tuned out to be 5.1 kDa for 1_PVL, 4.8 kDa for 1_PDL_4.8, 8.0 kDa for 1_PDL_8.0, derived from the degree of polymerization (DP) 49, 27, and 46 respectively. Considering the feed ratio of [VL or DL]/[1] = 50, these DPs were consistent with previous reports.^{5,9} Moreover, molecular weight distribution was sufficiently narrow around 1.1–1.2, meaning the polymerization proceeded in a controlled manner. Considering the above, since the appearance of 1_PVL was a white solid and that of 1_PDL was a colorless oily fluid, we have successfully synthesized the end-reactive polyester with either a crystalline or amorphous nature, which would be useful in material application to control thermomechanical properties.

Next, self-polyaddition of macromonomers 1_PVL and 1_PDL were studied (Scheme 2, Table 4). Since these polyester structures become liquid form at the reaction temperature of the Curtius rearrangement (~100°C),⁹ bulk conditions were chosen for this polyaddition to effectively proceed. First, 1_PVL was polymerized at 100°C for 1 h with/without DBTDL catalyst, and purified by precipitation into MeOH (Table 4, entries 1 and 2). As a result, the corresponding polyurethane poly(1_PVL) was successfully obtained in both reaction conditions, which was characterized by ¹H NMR and SEC measurement (Figures 3 and 4). Since the molecular weight of poly(1_PVL) did not show that much dependence on the existence of the catalyst, it turned out that this self-polyaddition of the macromonomer proceeded efficiently without any catalyst, at least under bulk condition. Next, the reaction with/without DBTDL catalyst was conducted overnight (Table 4, entries 3 and 4). As a result, the product showed around 25% higher M_n (16 kDa) compared with the ones obtained after 1 h reaction time (13 kDa), while the existence of the catalyst again did not impact the result much. Meanwhile, in case of the

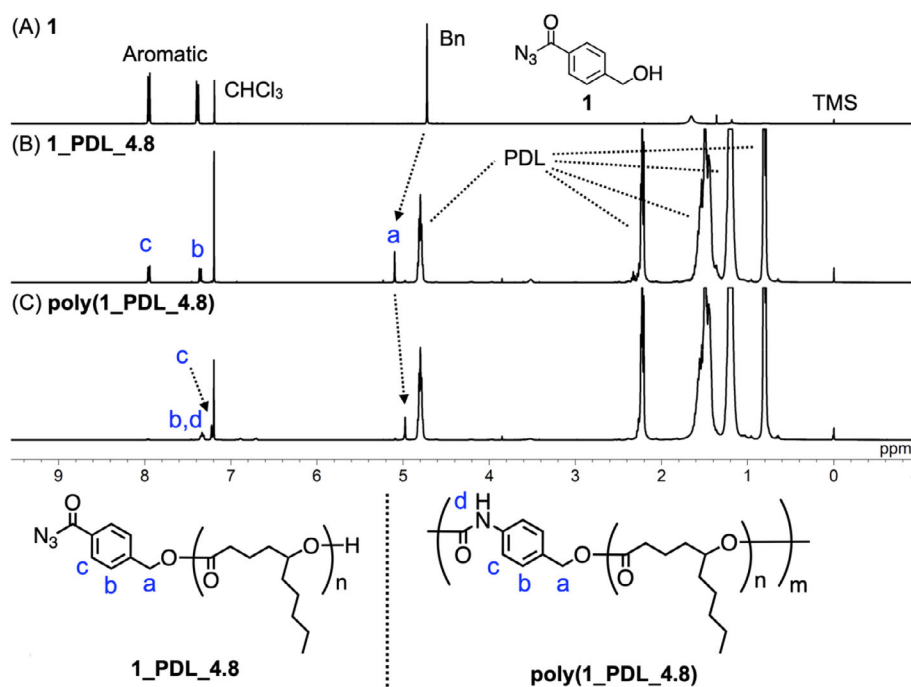


FIGURE 3 ^1H NMR spectra of (A) 1; (B) 1_PDL_4.8; (C) poly(1_PDL_4.8) (400 MHz, CDCl_3 , 298 K).

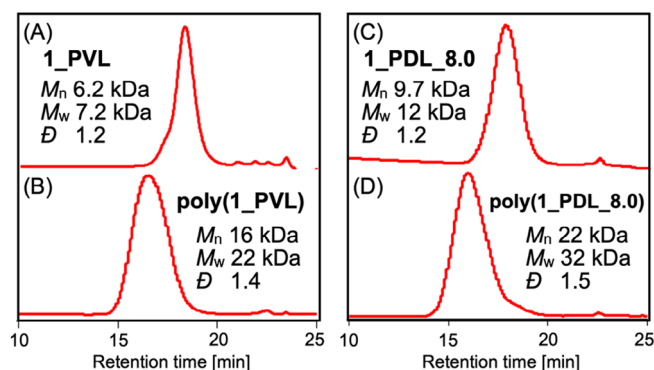


FIGURE 4 SEC profiles of (A) 1_PVL; (B) poly(1_PVL); (C) 1_PDL_8.0; and (D) poly(1_PDL_8.0) (eluent; THF, flow rate; 1.0 mL/min, 25°C).

self-polyaddition of 1, the long reaction time at high temperature caused undesired side reaction, resulting in the decomposition and low yield of polyurethane (Table 2, entry 3). Since such low yield and high molecular weight distribution were not observed here, undesired side reactions, which occurred on the self-polyaddition of 1, did not happen. Therefore, the reaction for 24 h and without catalyst was considered as a suitable condition for the self-polyaddition of macromonomers, and was applied on 1_PDL_4.8 and 1_PDL_8.0 (Table 4, entries 5 and 6). As a result, the corresponding polyurethane poly(1_PDL_4.8) and poly(1_PDL_8.0) were successfully obtained under both reaction conditions. However, interestingly, a shorter macromonomer 1_PDL_4.8 ($M_{n,\text{NMR}} = 4.8$ kDa) afforded a polyurethane with higher molecular weight ($M_n = 31$ kDa)

than the longer macromonomer 1_PDL_8.0 ($M_n = 22$ kDa). The reason of this phenomenon was speculated as follows. When the molecular weight of the macromonomer becomes higher, the reactivity of its end-group decreased, because the possibility of the collision of reactive groups becomes less. In case of entries 5 and 6, the lower reactivity of the polymer end-group on 1_PDL_8.0 played a dominant role despite the higher molecular weight of itself than 1_PDL_4.8, caused the higher molecular weight of the polyurethane from the latter. However, further detail of this phenomenon is difficult to be identified and out of the scope of this work. Herein, we have successfully synthesized novel polyurethane species from polyester macromonomers made of PVL (crystalline) and PDL (amorphous), by a simple bulk heating without any catalyst addition. Combining previously reported block copolymer synthesis (Figure 1A), the synthetic method based on 1_PVL or 1_PDL would enable synthesis of various polyurethanes, which has been difficult to be addressed by other methodologies.

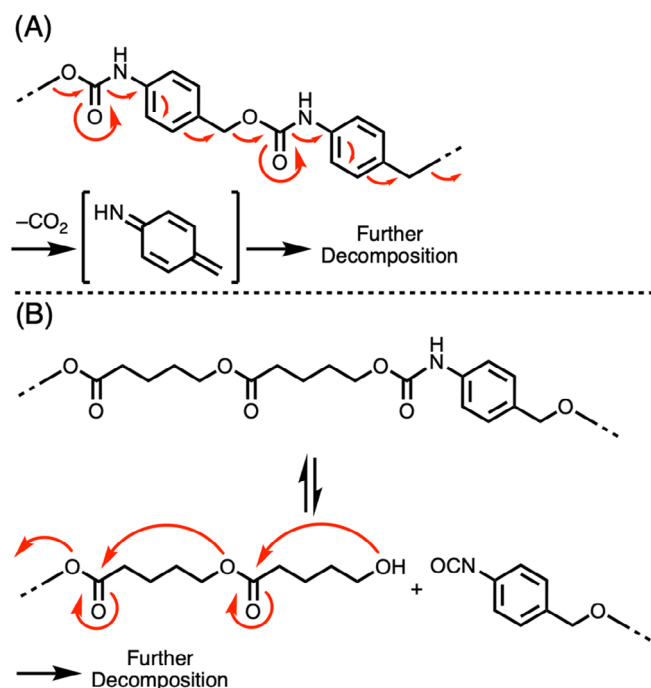
Finally, thermal analyses of the obtained polymers were conducted by TGA and DSC measurement (Table 5).⁸ As a result, 1_PVL and poly(1_PVL) showed similar T_m at around 50°C, while 1_PDL_4.8 and poly(1_PDL_4.8) showed similar T_g at around -50°C, which were consistent with typical PVL and PDL polymers.⁹ However, by a qualitative observation, polyurethane species showed a harder nature than for the macromonomers, meaning rheological analysis would provide more detailed information in this regard. Meanwhile, P1 did neither show T_g nor T_m , while it showed stepwise weight loss at high temperature, as observed by

TABLE 4 Reaction condition of polyaddition by Scheme 2.

Entry	Macromonomer	Cat.	Time [h]	Yield [%]	M_n [kDa] ^b	M_w [kDa] ^b	\bar{D}^b
1	1_PVL	- ^a	1	Quant.	13	20	1.5
2	1_PVL	DBTDL	1	63	13	17	1.3
3	1_PVL	DBTDL	24	65	16	22	1.4
4	1_PVL	- ^a	24	Quant.	16	23	1.4
5	1_PDL_4.8	- ^a	24	54	31	51	1.6
6	1_PDL_8.0	- ^a	24	89	22	32	1.5

^aNot added.^bCalculated by SEC (eluent; THF, flow rate; 1.0 mL/min, 25°C).**TABLE 5** Thermal parameters of polymers.

Polymer	T_g [°C] ^b	T_m [°C] ^b	T_{d5} [°C] ^c
P1	- ^a	- ^a	167
1_PVL	- ^a	54	172
Poly(1_PVL)	- ^a	53	151
1_PDL_4.8	-55	- ^a	258
Poly(1_PDL_4.8)	-45	- ^a	262

^aNot detected.^bEstimated by DSC (2nd heating).^cEstimated by TGA.**FIGURE 5** Plausible mechanism of the thermal degradation of (A) P1 via CO₂ elimination^{10a} and (B) poly(1_PVL).

TGA profile.⁸ The initial drastic weight drop observed at around 220°C was followed by a decrease after around 35% weight loss. Since CO₂ (48 Da) moiety occupies

around 32% weight of P1 (149 Da per repeating unit), this initial weight loss could be derived from the elimination of CO₂ gas from the polyurethane backbone structure. Afterwards, the weight loss proceeded again steeply from around 350°C until the complete decomposition. Such a two-step weight loss was only observed for P1, suggested its decomposition path way was different from other polymers. Based on previous studies on polyurethanes having similar repeating unit to P1, which showed a unique chain-decomposition path named “self-immolative depolymerization,”^{10a} the speculated decomposition mechanism of P1 is depicted and explained as followings (Figure 5A). Although the initiation point of the decomposition is unclear, once the CO₂ elimination occurred, the further degradation could proceed in a chain-depolymerization manner, probably promoted by the huge entropy gain by the elimination of CO₂. This chain-reaction path depicted in Figure 5A is only possible through the conjugative degradation path on P1 among the polymers tested in this work, resulted in a unique two-step decomposition. Meanwhile, poly(1_PVL) showed one step steep weight loss from 150 to 200°C, and afterwards the residue occupied only less than 10% weight, while such a decomposition was observed only higher than 300°C on poly(1_PDL_4.8),⁸ suggested the type of polyester backbone structure significantly affects their thermal stability. This observation was explained as following speculation. Considering the complete decomposition of 1_PVL proceeded much slower than that of poly(1_PVL),⁸ the latter would start from the reaction path relevant with urethane bond which does not exist in 1_PVL, and the plausible mechanism is depicted in Figure 5B. Namely, the repeating unit derived from 1 could somehow promote the depolymerization of PVL backbone to cause a rapid degradation which was not observed on the PDL counterpart and 1_PVL. This degradation would be initiated from the urethane bond cleavage, which provides the alcohol termination end of PVL to start back biting type depolymerization. Owing to the steric hindrance, the back biting path depicted in

Figure 5B would be more favorable in PVL than PDL, and the lower boiling point of VL (220°C) than DL (281°C) would also contribute to the rapid degradation of poly(1_PVL). Although further detail on the decomposition behavior is not proactively studied here, such a unique decomposition property would enable a certain contribution to the sustainable material use/production. Since self-immolative polymers have been intensively studied as an emerging class of degradable materials,^{10,11} this aspect could be focused on the polyurethane framework synthesized by alcohol tethering acylazide species, as demonstrated in this work.

3 | CONCLUSION

In this work, we investigated the utility of an orthogonal agent 1 to construct various type of polyurethane framework via macromonomer species synthesized by ROP initiated from the hydroxyl group of 1. Since PVL and PDL polymer backbones become liquid form at around 100°C for the Curtius rearrangement reaction, simple heating of the macromonomer species in a bulk condition afforded the corresponding polyurethane even without any additives. Such facile synthetic process could contribute to the development of precise polymer synthesis on polyurethane and its industrial application. Moreover, since further functionalization/derivatization on 1 can be easily applied, various type of functional polymer architectures could be designed based on this framework. Further studies along this line are currently ongoing in our group for contributing to the precise synthesis on polyurethane, which has been difficult to be addressed by the conventional synthetic method.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

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