

Accessing Chemically Recyclable Polyamides with Tunable Properties via Geminal Dimethyl Substitution

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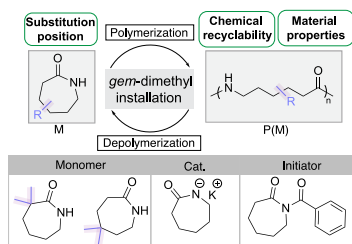
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Abstract: The development of new chemically recyclable polymers could serve as a means of reducing the plastic pollution and alleviating global energy crisis and monomer design strategy has driven the innovation in this field. In this contribution, α -dimethyl substituted caprolactam (α -DMCL) and γ -dimethyl substituted caprolactam (γ -DMCL) were prepared to evaluate the substitution position effect on chemical recyclability and material performance in polycaprolactam (PCL) system. The introduction of geminal dimethyl substitution to ϵ -caprolactam (CL) at α and γ position endowed the resulting polyamides P(α -DMCL) and P(γ -DMCL) with distinct thermal and mechanical properties. Remarkably, thermal depolymerization of P(γ -DMCL) in presence of potassium caprolactamate (CL-K) could be carried out at 200 °C and converted to γ -DMCL in 91% yield. The recovered γ -DMCL was capable of repolymerization to P(γ -DMCL) without a decrease in reactivity, demonstrating the proof-of-concept recyclability of P(γ -DMCL).

Graphical Abstract



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Key words: Ring-opening polymerization, monomer design, chemical recyclability, polyamides

1. Introduction

The overwhelming growth in global plastic production and use has caused the massive accumulation of plastic waste due to the nonbiodegradability of traditional petroleum-based plastics, leading to harmful environment impact.¹⁻³ Chemical recycling of polymer to monomer has been served as an attractive closed-loop economy to reduce the plastic pollution and alleviate the global energy crisis.⁴ The progress in catalytic methods and monomer design strategy has driven the innovation in chemically recyclable polymers. Polyamides having repeat units linked by amide bonds were ubiquitous both naturally and artificially. Proteins were critical polyamide biomolecules that played indispensable role for the structure, function, and regulation of the body. Synthetic polyamide has various physical characteristics such as chemical resistance, flexibility, and abrasion resistance that make it ideal for manufacturing and industrial applications. Polyamide 6 (PA6) also known as nylon 6 which was synthesized by ring-opening polymerization (ROP) of ϵ -caprolactam (CL) has emerged as a robust and versatile thermoplastic with widespread applications.^{5,6} Chemical recycling of PA6 to its monomer CL via ring-closing depolymerization (RCD) has been considered as an effective method to address the pollution of PA6 end-life. In fact, representative catalytic systems including 4-dimethylaminopyridine (DMAP), mixed alkali bases NaOH/KOH, **La1** ($\text{La}[\text{N}(\text{SiMe}_3)_2]_3$), and metallocene complex **La2** have been established to enable an efficient depolymerization of PA6 to CL (Figure 1a).⁶⁻¹¹ Despite the success of depolymerization, it required high temperature (>200 °C) due to the high melting processing temperature of PA6.

Monomer design strategy is shown to be a powerful approach to improving the chemical recyclability of polymer materials via modulating polymerization thermodynamics.¹²⁻¹⁴ By exploiting monomer design strategy, a number of polymer systems such as polyesters, polythioesters, polyacetals, and polycarbonates have accomplished effective closed-loop chemical recycling.¹⁵⁻³⁹ More importantly, this strategy also allowed for the regulation of polymer material performance, offering an opportunity to reconcile the conflicting polymer recyclability and material properties.⁴⁰ Particularly, the

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exploitation of geminal dimethyl substitution enabled the reversible polymerization and depolymerization of four-membered thiolactones and boosted the material performance of poly(3-hydroxybutyrate) (P3HB).^{41,42}

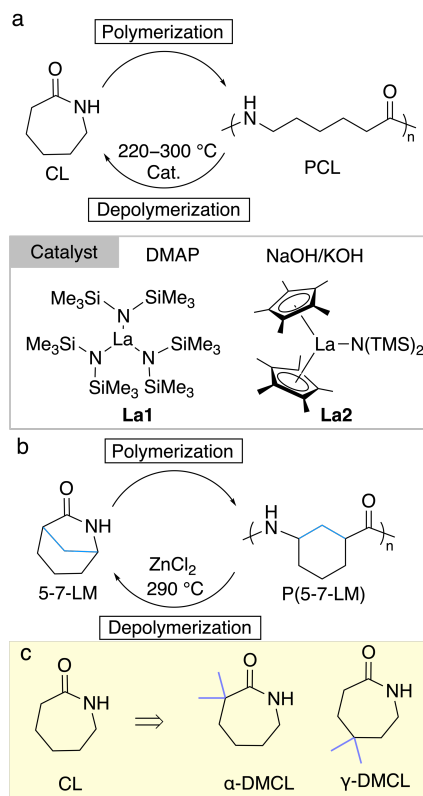


Figure 1. a) Chemical recycling of PCL to CL. b) Chemical recycling of P(5-7-LM) to 5-7-LM. c) Accessing chemically recyclable polyamides via geminal dimethyl substitution.

Despite significant advances in monomer design, it still remained less explored for the polyamide system. One pioneering breakthrough made by Chen and coworkers showcased the feasibility of ring-opening polymerization (ROP) of a bridged 5-membered and 7-membered lactam (5-7-LM) and subsequent recyclability to its monomer (Figure 1b).⁴³ In our previous work, we employed the geminal dimethyl substitution strategy to regulate the thermodynamic and material properties of 7-membered lactones.^{13,27} Inspired by this geminal dimethyl substitution strategy, we envisioned that installing geminal dimethyl substitution into CL would modulate the chemical recyclability of the resulting polycaprolactam (PCL) and deliver distinct material performance (Figure 1c) that are not accessible for PA6. Herein, two geminal dimethyl substituted CLs at α and γ position α -DMCL and γ -DMCL were prepared to probe the substitution position effect. Both monomers

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went through efficient polymerization, affording P(α -DMCL) and P(γ -DMCL) with number-average molecular weights (M_n) up to 90.5 kDa. The resulting PCLs demonstrated distinct thermal and mechanical properties, highlighting the significant influence of substitution position. Notably, an efficient depolymerization of P(γ -DMCL) could be achieved at 200 °C with potassium caprolactamate (CL-K) as the catalyst to produce a 91% yield of γ -DMCL in high purity which could undergo repolymerization to establish a closed-loop life cycle.

2. Experimental methods

2.1 Materials

All synthesis and manipulations of air- and moisture-sensitive chemicals and materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, on a high-vacuum line, or in an inert gas (Ar)-filled glovebox. High-performance liquid chromatography (HPLC)-grade anhydrous tetrahydrofuran (THF), hexanes, and diethyl ether (Et₂O) were dried via a Vigor YJC-5 solvent purification system and stored over activated Davison 4 Å molecular sieves in glovebox.

The reagents from Adamas-beta, Energy Chemical, and LeYan were used as received unless otherwise stated (NaH and KH was pre-purified in glovebox by using THF and n-hexane to wash the mineral oil). All solid monomers were recrystallized once from ethyl acetate (EA) and petroleum ether (PE) to get the crystals of monomers. The crystals were further purified by sublimation at 90 ~ 130 °C under vacuum.

2.2 Synthesis of polymer

Polymerization reactions were performed in glass reactors (4–10 mL) inside the glovebox for bulk polymerization runs. In a typical polymerization reaction, the catalyst, initiator, and monomers were added to the glass reactors. After stabilizing the temperature of metal bath, the glass reactors were heated by the hot metal bath. And when the reaction finished, cooling the glass reactors to RT and added the trifluoroethanol (2–3 mL) to quench the reaction, mixture was precipitated into 50 mL of acetone/ ethyl acetate, filtered, and washed with acetone/ ethyl acetate. This procedure was repeated twice to ensure any catalyst residue or unreacted monomer was removed. The polymer was dried in a vacuum oven at 60 °C to a constant weight.

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2.3 Characterization

2.3.1 Nuclear magnetic resonance spectroscopy

^1H NMR spectra were obtained on an Agilent 400-MR DD2 or Bruker AV II-400 MHz spectrometer at room temperature. (^1H : 400 MHz, ^{13}C : 100 MHz).

2.3.2 Size exclusion chromatography (SEC)

Measurements of polymer number-average molecular weight (M_n) and molecular weight distributions or polydispersity indices ($\mathcal{D} = M_w/M_n$) were performed via size exclusion chromatography (SEC). The SEC instrument consisted of an Agilent LC system equipped with one Shodex KF-G 4A guard column and two Shodex KF-805L 10 μm gel permeation columns and coupled with an Agilent G7162A 1260 Infinity II RI detector; The analysis was performed at 50 $^\circ\text{C}$ using HFIP with 0.05 M CF_3COONa as the eluent at a flow rate of 0.5 mL/min. The instrument was calibrated with 9 PMMA standards, and chromatograms were processed with Agilent OpenLab CDS Acquisition 2.5 molecular weight characterization software.

2.3.3 Thermal analysis

Melting-transition temperature (T_m) and glass-transition temperature (T_g) of purified and thoroughly dried polymer samples were measured by differential scanning calorimetry (DSC) on DSC25, TA Instrument. All T_m and T_g values were obtained from a second scan after the thermal history was removed from the first scan. The second heating rate was 10 $^\circ\text{C}/\text{min}$ and cooling rate was 10 $^\circ\text{C}/\text{min}$. Decomposition temperature (T_d) and maximum rate decomposition temperatures (T_{max}) of purified and thoroughly dried polymer samples were measured by thermogravimetric analyzer (TGA) on a TGA55, TA Instrument. Polymer samples were heated from ambient temperatures to 600 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C}/\text{min}$. Values of T_{max} were obtained from derivative (wt%/ $^\circ\text{C}$) vs. temperature ($^\circ\text{C}$) plots and defined by the peak values, while T_d values were obtained from wt% vs. temperature ($^\circ\text{C}$) plots and defined by the temperature of 5% weight loss.

2.3.4 Mechanical analysis

Tensile stress/strain testing was performed by an Instron 34SC-1 universal testing system. Samples were made by hot pressure in a steel mold ($50 \times 4 \times (0.4-0.8)$ mm³) and were

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stretched at a strain rate of 10 mm/min at ambient temperature until break. The measurements were performed 6–10 times for each test and the mechanical behavior reported are averaged from the measured data.

3. Results and discussion

Monomer synthesis

α -dimethyl substituted CL (α -DMCL) and γ -dimethyl substituted CL (γ -DMCL) were readily prepared on 10-gram scale according to modified procedures.^{44,45} Reductive cyclization of methyl 5-cyano-2,2-dimethylpentanoate via hydrogenation in the presence of Raney nickel and heating at 230 °C afforded α -DMCL in an overall yield of 35%. γ -DMCL was obtained from 4,4-dimethylcyclohexanone via *in situ* Beckmann rearrangement without purification of the oxime intermediate, which has been applied as a traditional method for the preparation of cyclic amides.⁴⁵ Their ¹H NMR spectra were consistent with the previously reported literature,^{46,47} confirming the correct structures.

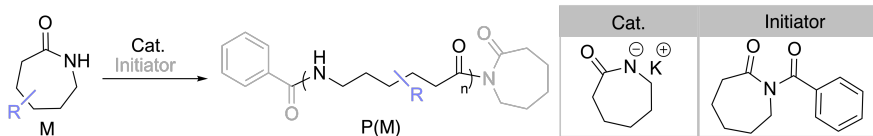
Polymerization study of CL-based monomers

Ring-opening polymerization of these CL-based monomers was investigated to elucidate the substitution effect. Initially, bases including alkali metal caprolactamates and the commercially available phosphazene base *t*-BuP₄ were screened as the catalysts for the ROP of γ -DMCL (Table S1), since they have been reported to be effective for the ROP of ϵ -lactams.⁴⁸ These polymerization reactions were carried out in DMF solution at 80 °C in presence of *N*-acyl substituted CL as the initiator. Potassium caprolactamate (CL-K) appeared to be the most active catalyst among these bases, facilitating the ROP of γ -DMCL to approach 61% conversions in 12 h (Table S1, entry 3). Continuingly, CL-K-mediated ROP of CL with a [monomer]/[catalyst]/[initiator] ([CL]/[CL-K]/[I]) ratio of 200/1/1 was conducted solvent-free in bulk at 160 °C, which gave 97% yield of P(CL) within 20 min (Table 1, entry 1). Size exclusion chromatography (SEC) analysis of this PCL sample in hexafluoroisopropanol (HFIP) revealed an M_n of 57.4 kDa and a polydispersity index (\mathcal{D}) of 2.44, which was much higher than the theoretical molecular weight. A 5-gram scale polymerization with a [CL]/[CL-K]/[I] ratio of 500/1/1 was next performed under a similar condition, resulting in 4.7 g of PCL with an improved M_n of 84.1 kDa (Table 1, entry 2). α -DMCL could proceed bulk polymerization at 120 °C with a [α -DMCL]/[CL-K]/[I] ratio of 200/1/1 and afford P(α -DMCL) in 50% yield. Increasing the [α -DMCL]/[CL-K]/[I] ratio to

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1000/1/1 led to an increase in M_n from 26.4 to 47.0 kDa (Table 1, entries 3 and 4). Under a similar condition, the bulk ROP of γ -DMCL at 120 °C produced 50% yield of P(γ -DMCL) with an M_n of 29.1 kDa and \mathcal{D} of 2.03 (Table 1, entry 5). It was worth noting that P(γ -DMCL) processed better solubility in DMF in comparison to PCL and P(α -DMCL). Subsequently, the ROP of γ -DMCL in DMF solution was carried out at 80 °C (Table 1, entries 6–8). γ -DMCL was able to reach 60% conversion and afford P(γ -DMCL) with a M_n of 90.5 kDa and a narrow \mathcal{D} of 1.50. Both P(α -DMCL) and P(γ -DMCL) were characterized by ^1H and ^{13}C NMR spectroscopy (Figures 2 and S6–9).

Table 1. ROP results of CL-based monomers.^a



Run	M	[M]/[Cat]/[I]	Conc. (M)	Temp. (°C)	Scale (g)	Time (h)	Yield ^b (%)	$M_{n,\text{Calcd}}^c$ (kDa)	M_n^d (kDa)	\mathcal{D}^d
1	CL	200/1/1	Bulk	160	0.3	20 min	97	22.3	57.4	2.44
2	CL	500/1/1	Bulk	160	5	1.5	94	53.5	84.1	2.63
3	α -DMCL	200/1/1	Bulk	120	0.3	3	50	14.5	26.4	1.57
4	α -DMCL	1000/1/1	Bulk	120	1	11	75	106.2	47.0	1.77
5	γ -DMCL	200/1/1	Bulk	120	0.3	5	50 ^e	14.5	29.1	2.03
6 ^f	γ -DMCL	200/1/1	5	80	0.2	15.5	63 ^e	18.1	61.3	1.51
7 ^f	γ -DMCL	500/1/1	5	80	0.3	56	34 ^e	24.3	77.4	1.49
8 ^f	γ -DMCL	500/1/1	6	80	2.5	90	60 ^e	42.7	90.5	1.50

^aCondition: Cat. = CL-K.

^bIsolated yield of the final collected polymer.

^c $M_{n,\text{Calcd}} = \text{MW}(\mathbf{M}) \times [\mathbf{M}]_0/[\mathbf{I}]_0 \times \text{conversion} (\%) + \text{MW}(\text{chain-end groups})$.

^dNumber-average molecular weight (M_n) and dispersity index ($\mathcal{D} = M_w/M_n$), determined by size exclusion chromatography (SEC) in HFIP at 50 °C or DMF at 40 °C.

^eMonomer conversion measured by ^1H NMR of the quenched solution.

^fSolvent = DMF.

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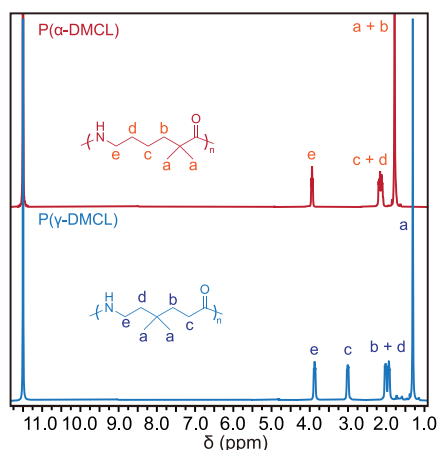
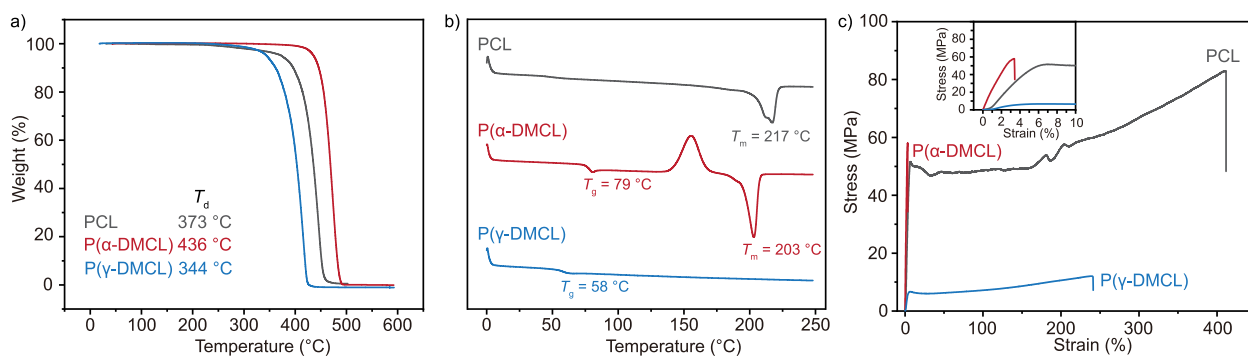


Figure 2. ^1H NMR spectra of P(α -DMCL) and P(γ -DMCL).

Thermal and mechanical property study

The thermal stability of these obtained polyamides was evaluated by thermal gravimetric analysis (TGA). In comparison to PCL having a decomposition temperature (T_d , onset decomposition temperature, measured by the temperature of 5% weight loss) of 373 °C, P(α -DMCL) exhibited an improved thermal stability with T_d of 436 °C and P(γ -DMCL) displayed a slightly lower T_d of 344 °C (Figure 3a). Differential scanning calorimetry (DSC) experiments were employed to examine the thermal properties of the obtained polyamides. As shown in Figure 3b, PCL was semicrystalline with a melting transition temperature (T_m) of 217 °C. Installing dimethyl substituent at α position rendered the resulting P(α -DMCL) with a clear glass transition temperature (T_g) of 79 °C and a T_m of 203 °C. In a sharp contrast, the absence of melting transition was observed for P(γ -DMCL) containing dimethyl groups at γ position, indicative of its amorphousness. P(γ -DMCL) only showed a T_g of 58 °C. The distinct thermal performance between P(α -DMCL) and P(γ -DMCL) highlighted the significance of substitution position.



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Figure 3. a) TGA curves of PCL, P(α -DMCL), and P(γ -DMCL). b) DSC curves of PCL, P(α -DMCL), and P(γ -DMCL). c) Strain-stress curves of PCL, P(α -DMCL), and P(γ -DMCL).

To further explore the mechanical property of the obtained polyamides, tensile testing was next investigated on their dogbone-shaped specimens prepared by hot pressing at 230 °C. The PCL sample prepared by [CL]/[CL-K]/[I] ratio of 1000/1/1 exhibited a remarkable tensile strength at break ($\sigma_B = 81 \pm 5$ MPa), an elongation strain at break (ϵ_B) of 407 % \pm 28%, and Young's modulus ($E = 1.13 \pm 0.081$ GPa), which was comparable to commercial nylon 6. Interestingly, P(α -DMCL) ($M_n = 47.0$ kDa, $D = 1.77$) having dimethyl substituents on α position showed a tensile strength of $\sigma_B = 55 \pm 4$ MPa with a limited strain ($\epsilon_B = 2.7\% \pm 0.4\%$) and Young's modulus ($E = 2.45 \pm 0.29$ GPa), representing a hard and brittle material. In contrast, P(γ -DMCL) displayed ductile thermoplastic behavior with ultimate elongation at break (ϵ_B) of 194% \pm 64% and tensile strength at break (σ_B) of 12 \pm 2 MPa (Figure 3c). Overall, the substituent position had a profound influence on the chemical and physical properties of the produced material.

Chemical recycling study

To elucidate the substitution effect on the chemical recyclability of these polyamides, PCL, P(α -DMCL), and P(γ -DMCL) were subjected to depolymerization study. Considering the good solubility of P(γ -DMCL) in DMF, the polymerization thermodynamics of γ -DMCL was first investigated using 2 mol% CL-K in DMF solution to monitor the polymerization equilibrium changes over a temperature range of 60 to 120 °C. According to the van't Hoff plot, the thermodynamic parameters were calculated to be $\Delta H_p^\circ = -10.7$ kJ mol⁻¹ and $\Delta S_p^\circ = -35.6$ J mol⁻¹ K⁻¹ (Table S3, Figure S5). Based on the equation $T_c = \Delta H_p^\circ / (\Delta S_p^\circ + R \ln [\gamma\text{-DMCL}]_o)$, the ceiling temperature T_c was calculated to be 27 °C at $[\gamma\text{-DMCL}]_o = 1$ M. This low T_c value suggested that chemical recycling of P(γ -DMCL) to γ -DMCL is thermodynamically feasible. To maximize polymer-catalyst contact and ensure uniform heating, P(γ -DMCL) and the catalyst were premixed in DMF and dried in vacuum prior to screening catalysts and catalytic conditions. Catalysts including CL-K, *t*-BuOK, MeOK, ZnCl₂, and La[N(SiMe₃)₂]₃ were examined for thermal bulk depolymerization of P(γ -DMCL) at 200 °C (Table 2). It was found that CL-K promoted the most efficient depolymerization to produce a 91% yield of γ -DMCL in 4 h among these catalysts. Encouraged by the high efficiency of CL-K, it was next investigated for the depolymerization

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of PCL and P(α -DMCL). CL-K-mediated bulk depolymerization of PCL was carried out at 240 °C and afforded 86% yield of CL in 5.5 h. Additionally, 35% yield of α -DMCL was recovered under a similar condition. It should be noted that a noticeable amount of oligomer impurity was accompanied with the recycled CL and α -DMCL. We hypothesized that the poor polymer-catalyst contact effectivity might be responsible for the decrease in depolymerization efficiency.

Table 2. Screening of depolymerization catalysts.^a

Run	Cat	Conc. (M)	[P]/[Cat]	Time (h)	Temp. (°C)	Yield ^b (%)
1	CL-K	Bulk	100/5	4	200	91
2	<i>t</i> -BuOK	Bulk	100/5	4	200	62
3	MeOK	Bulk	100/5	4	200	60
4	ZnCl ₂	Bulk	100/5	4	200	8
5	La[N(SiMe ₃) ₂] ₃	Bulk	100/5	4	200	11

^aCondition: P(γ -DMCL) = 60 mg, under vacuum.

^bCalculated based on the weight of collected monomers.

To establish the close-loop economy of P(γ -DMCL), γ -DMCL recovered from depolymerization of P(γ -DMCL) was tested for repolymerization with CL-K as the catalyst and *N*-acetyl caprolactam as the initiator. To our delight, recycled γ -DMCL underwent repolymerization with a [γ -DMCL]/[CL-K]/[I] ratio of 200/1/1 at 80 °C without a decrease in polymerization reactivity, approaching 73% conversion within 20 h (Table S5). In line with the result from starting P(γ -DMCL), the recycled P(γ -DMCL) displayed an M_n of 32.4 kDa and a D of 1.98. These findings highlighted the feasibility and efficiency for chemical recycling of P(γ -DMCL). More impressively, CL-K could be recycled as the depolymerization catalyst. To explore the recyclability of catalyst CL-K, the remained CL-K after a depolymerization process was recharged with 200 mg of fresh P(γ -DMCL) for the 2nd round depolymerization use (Table S6). 84% yield of γ -DMCL was recovered under a similar condition, manifesting the recyclability of catalyst CL-K.

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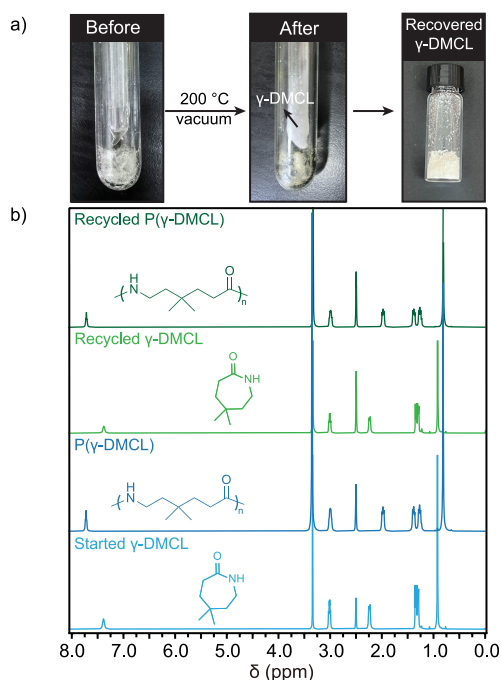


Figure 4. Chemical recycling study of P(γ -DMCL). a) Photo images of the recycling set-up before and after depolymerization. b) ^1H NMR spectra of started γ -DMCL, P(γ -DMCL), and recycled γ -DMCL, and recycled P(γ -DMCL).

4. Conclusions

Toward our goal of developing chemically recyclable polyamides, two geminal dimethyl substituted CLs at α and γ position were prepared to probe the change of their thermodynamic parameters for ROP and depolymerization and material performance. Both monomers were subjected to efficient polymerization, affording P(α -MDCL) and P(γ -MDCL) with different thermal and mechanical properties: P(α -MDCL) represented a hard and brittle material with a high T_m of 203 °C while P(γ -MDCL) behaved as a ductile thermoplastic. Their chemical recycling study revealed that P(γ -DMCL) could be efficiently and selectively recycled back to γ -DMCL. This study explored the application of geminal dimethyl substitution strategy in chemically recyclable polyamides and allowed access to diversified and different polyamide products.

Authorship contribution statement

Jia-Hao Chen and Yi-Min Tu: designed and performed experiments related to monomer, catalyst, and polymer synthesis, designed and performed the characterization experiments, performed the depolymerization experiments. **Jia-Rong Yao, Xiang-Ting Tang, and Yun-Yun Xia:** performed experiments related

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to monomer and catalyst synthesis. **Zhongzheng Cai and Qi Zhang**: directed the research. **Jian-Bo Zhu**: conceived the project, directed the research.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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