

Green Synthesis of Chemically Recyclable Polyesters via Dehydrogenative Copolymerization of Diols

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 Electronic Supplementary Information

Abstract Preparation of chemically recyclable polyesters by ring-opening polymerization (ROP) has made a considerable progress over the past few years. However, this method involves cumbersome synthesis and minimal functional diversity of cyclic monomers. Therefore, it is of great significance to develop novel polymerization methods for direct polymerization of commercially available monomers to prepare recyclable polyesters with versatile functionalities. In present work, we report dehydrogenative copolymerization of commercial α,ω -diols to afford high molecular weight chemically recyclable aliphatic copolyesters ($65.7 \text{ kg}\cdot\text{mol}^{-1}$) by using commercially available Milstein catalyst precursor. The thermal properties of the obtained copolymers could be finely tuned by simply adjusting the feeding ratio of two monomers. The incorporation of aliphatic or aromatic rings into polyester mainchain *via* copolymerization of 1,10-decanediol with 1,4-cyclohexanedimethanol and 1,4-benzenedimethanol could significantly improve the thermal properties of the resulting copolymers. More importantly, the obtained copolyesters were able to completely depolymerize back to original diols *via* hydrogenation by the same catalyst in solvent-free and mild conditions, thus offering a green and cost-effective route toward the preparation of widely used polyesters.

Keywords Chemically recyclable; Dehydrogenative copolymerization; Polyester; Diol

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INTRODUCTION

With the rapid development of industrialization, polymers have become indispensable basic materials for modern society.^[1] While polymeric materials provide convenience to human life, they have also led to increasingly environmental issues such as “white pollution” and “microplastics”, as well as consumption of energy due to incumbent commodity plastics mainly originate from fossil resources.^[2–4] Some commercially available biodegradable polyesters such as PLA, PBS and P3HB have partially addressed these problems, but these kinds of polymers are generally not as strong or cheap to make as fossil-based plastics and also difficult to complete degradation at realistic environmental conditions.^[5–9] Therefore, utilizing renewable resources for preparation of chemically recyclable polymers to replace their petrochemical counterparts have aroused much attention and concern in recent years.

It is a fascinating strategy to improve the recyclability of

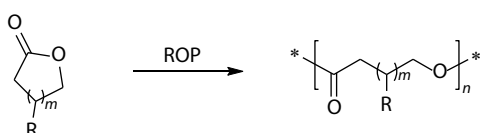
polymeric materials *via* embedding cleavable groups into polymer chains. The labile ester moiety has often been used to perform this task.^[10,11] Polyester contains a large number of repeated ester units in polymer backbone, thus possessing excellent degradability and recyclability at low energy levels.^[12] Recently, the development of chemically recyclable polymers with desirable properties has made a tremendous progress.^[13–18] Chen and coworkers documented a series of butyrolactone-derived recyclable polyesters with excellent thermomechanical properties and chemical recyclability.^[19–25] Lu *et al.* also reported the synthesis of chemically recyclable polyesters by ROP of the functionalized butyrolactones. Hillmyer,^[26] Hoyer^[27] and Li^[28,29] reported respectively preparations of recyclable polyvalerolactones bearing different functional groups *via* ROP utilizing organocatalysts. Nevertheless, the ROP method still faces formidable challenges such as minimal functional diversity of cyclic monomers, cumbersome synthesis steps and lower polymerization temperature.^[29] Therefore, it is of great significance to develop novel polymerization methods for achieving direct polymerization of commercially available monomers at higher temperatures to prepare chemically recyclable polyesters with versatile

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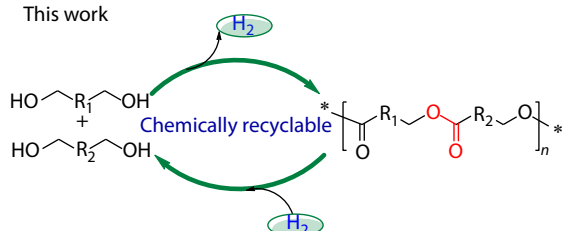
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Previous work



- ✗ Cumbersome monomer synthesis
- ✗ Few functional diversity
- ✓ Highly atomic economy
- ✓ Excellent controllability

This work



- ✓ Commercial monomers
- ✓ Simply chemical recycling
- ✓ Only byproduct H₂
- ✓ Structure adjustable

Scheme 1 Polymerization methods of chemically recyclable polyesters.

functionalities (Scheme 1).

In 2005 and 2007, Milstein's group reported catalytic dehydrogenative homo-coupling of primary alcohols to esters and cross-coupling of alcohols/amines to amides respectively, *via* metal-ligand cooperation by using a pincer-type pyridine-based ruthenium complexes.^[30–32] These reactions are green and sustainable because the only byproduct H₂ can be used as a new type of energy. Using this highly efficient catalytic system, Guan^[33] and Milstein group^[34] realized directly dehydrogenative polymerization of diols and diamines to polyamides, Robertson *et al.*^[35] reported dehydrogenative polymerization of a series of aliphatic diols to afford corresponding high molecular weight polyesters for the first time. In the meanwhile, the specific systems can also catalyze hydrogenation of the obtained amides, esters as well as the corresponding polymers back to the original alcohols and amines,^[36–39] thus providing a new strategy to prepare chemically recyclable polymers. However, the few reports are limited to dehydrogenative homopolymerization of aliphatic diols and hydrogenative depolymerization of some commercial polyesters. No copolymerization and circular monomer-polymer-monomer cycles have been investigated *via* dehydrogenative polymerization and/or hydrogenative depolymerization processes. Herein, we further demonstrate dehydrogenative copolymerization of commercially available diols to afford high performance copolyesters and their hydrogenative depolymerization back to the pristine diols by using Milstein catalyst. The thermal properties of the obtained copolyesters can be finely tuned by regulating the structures and feeding molar ratios of monomers. More strikingly, the obtained copolyesters could be quantitatively depolymerized back to the original diols catalyzed by the same catalyst in solvent-free and mild conditions, demonstrating a “zero emission” closed-loop cycle at the proof-of-concept level.

EXPERIMENTAL

General Considerations

All manipulations of air-sensitive chemicals and materials were carried out with the rigorous exclusion of oxygen and moisture under an atmosphere of nitrogen using standard Schlenk techniques or in a nitrogen gas filled M. Braun glovebox. Toluene was purified using an SPS Braun system. Tetrahydrofuran (THF) was purified by distillation over sodium with benzophenone as indicator under a nitrogen atmosphere. Other solvents and monomers were dried over calcium hydride with stirring for 48 h and distilled before use. The Milstein catalyst was synthesized according to the literature procedure.^[26] All diols were purchased from Shanghai Haohong Scientific Co., Ltd. Deuterated NMR solvents were purchased from Cambridge Isotopes, dried over Na (for C₆D₆) and molecular sieve (for CDCl₃), and stored in the glovebox. NMR spectra were recorded at 400 MHz (¹H), 101 MHz (¹³C) and 162 MHz (³¹P) using a Bruker Avance-400 NMR spectrometer. ¹H-NMR chemical shifts were referenced to the residual hydrogen signals of the deuterated solvents (7.26 ppm, CDCl₃; 7.16 ppm, C₆D₆), and the ¹³C-NMR chemical shifts were referenced to the ¹³C signals of the deuterated solvents (77.16 ppm, CDCl₃; 128.06 ppm, C₆D₆). Molecular weight (*M_n*) and molecular weight distribution (*M_w/M_n*) of the polymers were measured by means of gel permeation chromatography (GPC) on a TOSOH HLC-8420 GPC instrument at 40 °C against polystyrene standards. Melting transition (*T_m*) and glass transition (*T_g*) temperatures were measured by differential on a Mettler TOPEM TM DSC Instruments under nitrogen atmosphere. All *T_m*s and *T_g*s were obtained from a second scan after the thermal history was removed from the first scan. The second heating and cooling rates were 10 °C/min. The onset decomposition temperatures (*T_d*, defined at 5% weight loss) of the polymers were measured by thermal gravimetric analysis (TGA) on a SDTQ 600, TA instruments. Polymer samples were heated from ambient temperatures to 600 °C at a rate of 20 °C/min.

Typical Polymerization Procedure

In glovebox, the Milstein catalyst precursor (9.8 mg, 0.02 mmol), KO^tBu (2.2 mg, 0.02 mmol) and anisole (1.0 mL) were added to a 100 mL Schlenk flask, and the mixture was stirred for 5 min at room temperature to activate the catalyst precursor. An anisole (2.0 mL) solution of diols (10.0 mmol for homopolymerization, different monomers feeding molar ratios for copolymerization with a total monomer contents of 10.0 mmol) was added to the flask. After taking out glovebox, the Schlenk flask was connected to a nitrogen-filled balloon and was rapidly heated to 150 °C for 5 h. Following this initial period, the reaction mixture was put under vacuum for an additional 67 h. After a desired time period, the flask was cooled down to room temperature, the reaction mixture was dissolved in a minimum amount of THF and precipitated in methanol. The resulting polymer was dried under vacuum to constant. The polymer yield was 91.2% determined by weight (Table 1, entry 3). *M₂* conversion rate calculation method: the molar content of the two monomers in the copolymer was calculated by ¹H- and quantitative ¹³C-NMR spectra, the weight of *M₂* in the copolymer is then calculated from the yield of the polymer, Conv. = *M₂*/*M₂'* (*M₂* = the weight of *M₂* in the copolymer, *M₂'* =

Table 1 Copolymerization of different diols catalyzed by Milstein catalyst.^a

R = R₁ or R₂

Entry	Monomers	[M ₁]/[M ₂] ^b	M ₁ /M ₂ ^c	Conv. ^d (%)	Yield (%)	M _n ^e (kg/mol)	M _w /M _n ^e	T _m ^f (°C)	T _g ^f (°C)
1 ^g	[[Pe]	100/0	100	23.2	23.2	20.0	1.5	33.9	n.d.
2 ^g	[He]	100/0	100	69.6	69.6	31.4	1.9	43.0	n.d.
3 ^g	[De]	100/0	100	91.2	91.2	65.7	2.0	71.7	n.d.
4 ^g	[Cy]	100/0	100	71.7	71.7	26.9	2.2	n.d.	55.4
5 ^g	[T-Cy]	100/0	100	90.2	90.2	23.3	1.6	n.d.	67.4
6 ^g	[Be]	100/0	100	84.8	84.8	2.0	4.1	n.d.	76.9
7	[De]/[Pe]	20/80	22.3/77.7	31.3	32.5	29.6	1.8	38.4	n.d.
8	[De]/[Pe]	40/60	47.6/52.4	53.6	63.2	19.6	1.7	53.0	n.d.
9	[De]/[Pe]	50/50	54.1/45.9	61.7	68.6	20.9	1.7	53.2	n.d.
10	[De]/[Pe]	60/40	65.8/34.2	61.6	81.1	39.8	2.0	61.1	n.d.
11	[De]/[Pe]	80/20	79.4/20.6	86.2	83.5	49.6	2.0	62.8	n.d.
12	[De]/[He]	20/80	22.7/77.3	65.6	80.2	38.9	2.2	43.5	n.d.
13	[De]/[He]	40/60	43.1/56.9	64.3	65.5	17.4	1.5	51.2	n.d.
14	[De]/[He]	50/50	54.1/45.9	69.4	78.8	12.6	1.4	54.4	n.d.
15	[De]/[He]	60/40	63.7/36.3	74.1	83.3	44.7	1.9	57.8	n.d.
16	[De]/[He]	80/20	81.3/18.7	80.1	85.9	49.1	2.3	64.2	n.d.
17	[Cy]/[De]	20/80	17.4/82.6	42.6	70.5	65.9	2.2	51.2	n.d.
18	[Cy]/[De]	40/60	40.1/59.9	55.1	68.9	39.3	2.0	26.0	n.d.
19	[Cy]/[De]	50/50	47.5/52.5	62.5	71.0	29.9	1.9	12.4	n.d.
20	[Cy]/[De]	60/40	60.1/39.9	78.6	61.8	27.7	1.9	n.d.	-29.1
21	[Cy]/[De]	80/20	81.3/18.7	78.2	79.8	13.2	1.6	n.d.	3.2
22	[T-Cy]/[De]	20/80	15.3/84.7	81.3	83.1	42.4	2.4	47.7	n.d.
23	[T-Cy]/[De]	50/50	48.3/51.7	89.8	89.5	51.8	2.8	9.1	n.d.
24	[T-Cy]/[De]	80/20	81.2/18.8	88.2	83.9	34.2	2.9	n.d.	13.6
25	[Be]/[De]	9.0/91.0	9.8/90.2	63.9	76.1	22.8	2.2	57.5	n.d.
26	[Be]/[De]	33.3/66.7	32.1/67.9	71.4	74.4	23.5	2.1	35.7	n.d.

^a General conditions: 10 mmol diols, 0.02 mmol Milstein catalyst precursor and 0.02 mmol KO^tBu, 3 mL of anisole, 150 °C, 72 h. Pe, 1,5-pentandiol; He, 1,6-hexandiol; De, 1,10-decanediol; Cy, 1,4-cyclohexanedimethanol; T-Cy, *trans*-1,4-cyclohexanedimethanol. Be, 1,4-Benzenedimethanol; ^b Feeding molar ratio; ^c Copolymer composition calculated by ¹H-NMR (25, 26) or quantitative ¹³C-NMR (7–24) spectra; ^d Conversion rate of diol (entries 1–6), conversion rate of M₂ (entries 7–16), conversion rate of M₁ (entries 17–26); ^e Determined by gel permeation chromatography (GPC) using polystyrene standards; ^f Determined by differential scanning calorimetry (DSC); ^g 100/0 represents homo-polymerization; n.d., not detected.

M₂ feeding weight).

Typical Hydrogenative Depolymerization Procedure

Hydrogenation in toluene

The Milstein catalyst precursor (9.8 mg, 0.02 mmol), KO^tBu (2.2 mg, 0.02 mmol) and poly(De-co-Cy) (318.0 mg, 2.0 mmol; Table 1, entry 19) were dissolved in 1.0 mL of toluene. The reaction mixture was transferred to an autoclave and pressurized with H₂ (1.2 MPa). The autoclave was heated at 120 °C under continuous stirring for 48 h. After the desired time period, the autoclave was cooled down to room temperature and the H₂ gas was slowly vented off in a fume hood. The solvent was removed under reduced pressure and 295.7 mg recovered monomers were obtained (93%) and analysed by NMR spectra.

Hydrogenation under solvent-free condition

The Milstein catalyst precursor (9.8 mg, 0.02 mmol), KO^tBu (2.2 mg, 0.02 mmol) and poly(De-co-He) (300.0 mg; Table 1, Entry 15) were added to the autoclave under nitrogen atmosphere. The autoclave was heated at 120 °C under continuous stirring for 48 h. After the desired time period, the autoclave was cooled down to room temperature and the hydrogen gas was slowly vented off in a fume hood. The white crystals were adhered to the inner wall of autoclave, no further separation was required. The yield

of the recovered monomers was 93%, which were analysed by NMR spectra.

Hydrolysis procedure

The copolymer (500.0 mg), KOH (50.0 mg, 10 wt%) and a given solvent (H₂O/THF) were added to a 100 mL round-bottom flask, the mixture was refluxed under continuous stirring for 48 h. After the reaction time was completed, the flask was cooled down to room temperature and 2 mol/L HCl aqueous solution was added to neutralize the excess KOH and acidize the produced carboxylates. The mixture was extracted with CH₂Cl₂ (3 × 50 mL), the combined organic phase was dried over MgSO₄ and subsequently all volatiles were removed under reduced pressure. The residue was detected by NMR spectra.

Kinetic Experimental Procedure

Copolymerization process

In glovebox, the Milstein catalyst precursor (19.6 mg, 0.04 mmol), KO^tBu (4.4 mg, 0.04 mmol) and anisole (2.0 mL) were added to a 100 mL Schlenk flask, and the mixture was stirred for 5 minutes at room temperature to activate the catalyst precursor. An anisole (4.0 mL) solution of De (10.0 mmol, 1.74 g) and Cy (10.0 mmol, 1.44 g) was added to the flask. After taking out glovebox, the Schlenk flask was connected to a nitrogen-

filled balloon and was rapidly heated to 150 °C for 1 h, then the reaction was cooled down to room temperature and sampled under nitrogen condition to keep the reaction system in a strictly inert gas atmosphere. Keep on reacting and repeated the sampling operation to take samples at 3 h, 5 h, 7 h, 9 h in sequence. The obtained samples were detected by $^1\text{H-NMR}$ spectra.

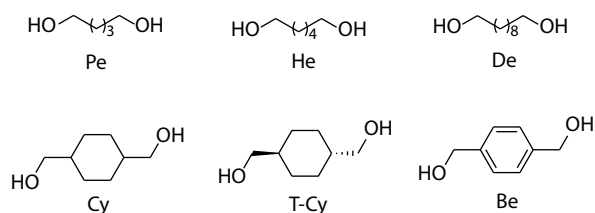
Depolymerization process

The Milstein catalyst precursor 2 mol%, KO^tBu 2 mol% and $\text{poly(De)/poly(Cy)}=1/1$ were dissolved in 2.0 mL of toluene. The reaction mixture was transferred to an autoclave and pressurized with H_2 (1.2 MPa). The autoclave was heated at 120 °C under continuous stirring for 1 or 4 h, respectively. After a desired time period, the solvent was removed under vacuum and the product was detected by $^1\text{H-NMR}$ spectra.

RESULTS AND DISCUSSION

The commercially available Milstein catalyst precursor was used to catalyze the dehydrogenative homo- and co-polymerization of diols to polyesters. We initially investigated the homopolymerization of different kinds of diols, including aliphatic diols and aliphatic/aromatic ring- containing diols as presented in Scheme 2. When using 1,4-butanediol as monomer, the starting material was completely converted to γ -butyrolactone and no polyester was detected. Switching monomer to 1,5-pentanediol (Pe), the desired polymer was obtained in a low yield of 23.2% along with formation of δ -valerolactone. Further increasing the length of aliphatic diols, the polymerization proceeded smoothly and corresponding polyesters were produced successfully in both 1,6-hexanediol (He) and 1,10-decanediol (De) cases. As shown in Table 1 (entries 1–3), the T_m of the homopolymer increased with the spacer length of diol, probably owing to the superior crystallinity of the long chain diol. This is in line with Robertson's report.^[35]

From $^1\text{H-NMR}$ spectrum of poly(Pe) (Fig. S1 in the electronic supplementary information, ESI), we could find two multiplets at 4.07 and 2.36 ppm corresponding to the methylene moieties of $-\text{CH}_2\text{C}(\text{O})\text{OCH}_2-$ and $-\text{CH}_2\text{C}(\text{O})\text{OCH}_2-$, respectively (entry 1). Interestingly, the two similar sets of peaks were shown as clear triplets in the $^1\text{H-NMR}$ spectrum of poly(De) (Fig. S5 in ESI), perhaps meaning the different microstructures of these two homopolymers (entry 3). In fact, every α,ω -diol can generate three kinds of linkages depending on the monomer addition mode [head-to-head (HH), head-to-tail (HT) and tail-to-tail (TT)] (Fig. 1). This different linking mode will lead to chemical inequivalence of each kind of ester moiety, which displayed as complex peak patterns in the $^1\text{H-NMR}$ spectrum of poly(Pe). The connection effect is able to be com-



Scheme 2 Structures of different diols used in present work.

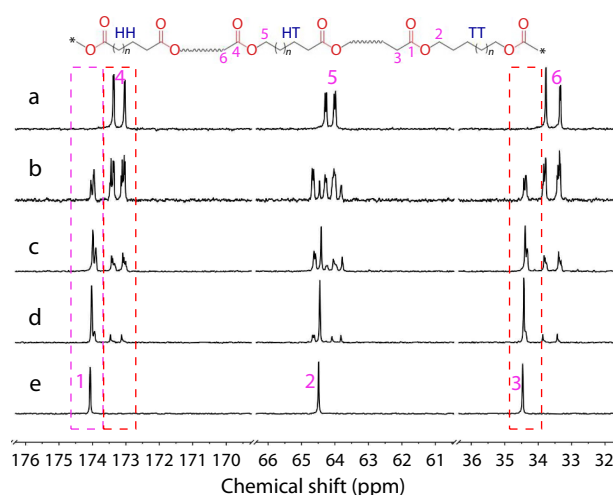


Fig. 1 Quantitative $^{13}\text{C-NMR}$ spectra of poly(De-co-Pe)s. (a–e) corresponding to entries 1, 7, 9, 11, 3 in Table 1, respectively; HT: head-to-tail, HH: head-to-head, TT: tail-to-tail.

pensated by the long spacer in poly(De), thus its $^1\text{H-NMR}$ spectrum still exhibited triplets in the corresponding locations. In addition, the quintet at 1.94 ppm is attributed to the protons between two ester groups ($-\text{OC}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}-$) originated from HH structural unit, and there are equal integration of proton signals appearing at 1.40 ppm, which is assigned to $-\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OC}(\text{O})-$ moieties derived from TT structural unit (Fig. S1 in ESI). This result indicated that the content of HH linkage is always equal to that of TT linkage. Accordingly, the equation $[\text{HT}]/([\text{HH}]+[\text{TT}]+[\text{HT}]) = (I_{4.07} - 2I_{1.40})/I_{4.07}$ calculates the molar fraction of HT linkage in poly(Pe) approximately as 1/2, where $I_{4.07}$, $I_{1.40}$ are the integrations of protons appearing at chemical shifts of 4.07 and 1.40 ppm, respectively. The calculation result of $[\text{HH}]+[\text{TT}]=[\text{HT}]$ suggested that the transformation of hydroxy into carbonyl group completely obeys the statistical principle, thus causing a regioirregular polymer. This result was further confirmed by the hydrolysis experiment ut infra (Figs. S67 and S68 in ESI). As displayed in Fig. 1(a), all three sets of carbon signals at 173.20, 64.14 and 33.48 ppm assigned to the carbons 1, 2 and 3 exhibited two multiplets with approximate integration ratio of 1:1 referring to the different chemical environments of every kind of carbons.

It is well known that polymer containing ring structures in mainchain can significantly improve its thermal properties, thus we further expanded the monomer to 1,4-cyclohexanedimethanol (Cy), *trans*-1,4-cyclohexanedimethanol (T-Cy) and 1,4-benzenedimethanol (Be). As depicted in Table 1 (entries 4–6) (Scheme 2), no T_m s were detected in these kinds of ring-containing polyesters, meaning their amorphous properties. However, the T_g increased from 55.4 °C to 76.9 °C as the crystallinity and stiffness of monomer increased, and all T_g s are much higher than those of their aliphatic counterparts, although the molecular weight of homo-poly(Be) was only 2000 g/mol (Table 1, entry 6). For example, the T_g of commercial PCL is only about -60 °C. With these results in hand, we hoped to improve the thermal properties of relevant polyesters through copolymerization of different diols with long-

chain or ring-containing diols. The corresponding experimental results are also summarized in Table 1. All these copolymers exhibited good thermodynamic stabilities and their T_{ds} and $T_{max,s}$ are above 350 °C (Fig. S66 in ESI).

The long-chain 1,10-decanediol was firstly chosen as comonomer to incorporate into the polyester derived from 1,5-pentanediol or 1,6-hexanediol, which could be made from the sustainable cellulose-based platform compounds furfural or 5-hydroxymethylfurfural. Compared with long-chain diols, 1,5-pentanediol is preferential to form thermodynamically stable and kinetically favorable δ -valerolactone over the desired polyester, thus leading to low polymer yield (Table 1, entry 1). Surprisingly, when 1,10-decanediol as comonomer was added, the conversion of 1,5-pentanediol increased from 31.3% to 90.4% with the increase of monomer feeding molar ratio ([De]/[Pe]) from 20/80 to 80/20, which was much higher than that in the homopolymerization (23.2%), probably due to incorporation of 1,10-decanediol impedes the intramolecular dehydrogenative esterification of 1,5-pentanediol to form δ -valerolactone during the copolymerization process. The incorporation rate of each monomer could be calculated by both proton and quantitative ^{13}C -NMR spectra. In the ^1H -NMR spectra of poly(De-co-Pe)s, two sets of signals at the range of 2.40–2.20 ppm are ascribed to the $-\text{CH}_2\text{C}(\text{O})\text{O}-$ groups derived from Pe and De monomers respectively, but a few overlaps affect the accuracy of integrations, thus all of the copolymer composition data exhibited in Table 1 were determined by quantitative ^{13}C -NMR spectra. Fig. 1 clearly presented minor chemical shift deviations of the same kind of carbons originated from different monomers and linking modes. The carbonyl signals derived from the long chain 1,10-decanediol appeared downfield compared with those derived from the short-chain monomer 1,5-pentanediol. With the increase of De content in polymer, the related carbonyl peak intensities increased gradually. The unimodal distribution of GPC curve meant that two monomers were successfully incorporated into one polymer chain rather than the mixture of two homopolymers (Fig. 2, red line). In addition, the molecular weight and thermal properties of these copolymers were different from those of both homopolymers as the result of random copolymerization of two monomers. It is interesting that the incorporation rate of two monomers was nearly equivalent to the monomer feeding ratio, probably attributing to the close

reactivity ratio of two monomers in present polymerization system. Therefore, the composition of the resultant copolymer could be precisely tuned by simply changing the monomer feeding molar ratio (Fig. 1). As expected, the thermal property of the copolymer was greatly enhanced when 1,10-decanediol was incorporated, the T_m s increased from 33.9 °C to 62.8 °C when monomer feeding ratio changed from 0 to 80/20 (Fig. S62 in ESI).

We further studied the copolymerization behaviors of 1,6-hexanediol and 1,10-decanediol, the corresponding data are displayed in Table 1 (entries 12–16). 1,6-Hexanediol was converted into related polyester in a moderate yield of 69.6%, ϵ -caprolactone was not detected in the reaction system, perhaps because of its ring strain. The T_m of poly(He) (43.0 °C) is much lower than that of polycaprolactone (PCL, 59–64 °C) generated from ROP of ϵ -caprolactone, indicative of the different microstructures of these two types of polymers. In fact, each He can generate three kinds of ester linkages depending on the addition mode (HH, HT, or TT). Only HT mode generates the ester linkages identical to those of PCL. The regioirregular polyester backbones disrupt the crystallinity of poly(He) and thus decrease its T_m . Nonetheless, the lost thermal property could be compensated by incorporation of 1,10-decanediol into the polymer chain. When the feeding molar ratio of [De]/[He] reached 80/20, the T_m of the resulting copolyester was 64.2 °C, nearly equivalent to that of PCL. The thermal properties of the copolymers could be tuned by regulating copolymer composition. As shown in Table 1, when De content in the copolymer increased from 0% to 81.3%, the T_m s of the copolymer varied from 43.0 °C to 64.2 °C accordingly (Fig. 3).

As aforementioned, the thermal and mechanical properties of aliphatic polyesters are not enough to satisfy the needs of versatile applications, introducing aliphatic or aromatic rings into polymer chain is expected to address this problem. Therefore, we further investigated the copolymerization of 1,10-decanediol with 1,4-cyclohexanedimethanol as well as the thermal properties of the resulting polyesters (Table 1, entries 17–21). The homopolymer derived from the mixture of *cis*- and *trans*-1,4-cyclohexanedimethanol (Cy) has a T_g of 55.4 °C, which is much higher than that of poly(De), and no T_m was found in DSC curve. When Cy was used as a comonomer to be incorporated into poly(De) chain, the thermal

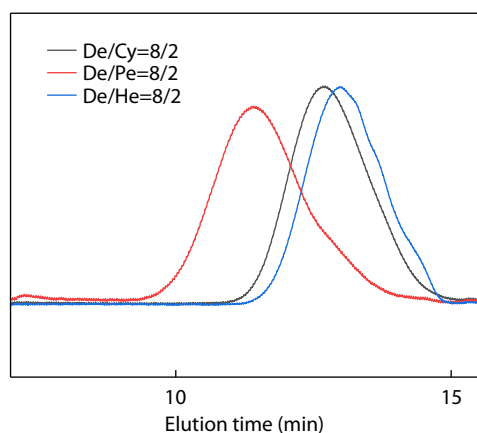


Fig. 2 GPC curves of the selected copolyesters.

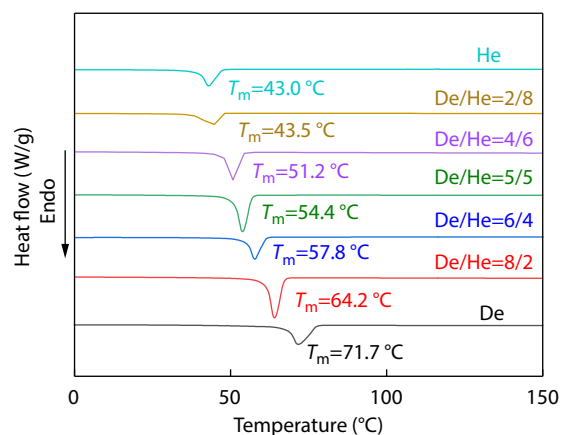


Fig. 3 DSC curves of poly(De-co-He)s.

properties of the resultant polymers have significant changes. Increasing the feeding ratio of [Cy]/[De] (Table 1, entries 17–19), the obtained copolyesters exhibit gradually decreased T_m values. When the content of Cy reached 48.5 mol%, the resulting copolymer displayed a T_m of 12.4 °C, which is much lower than that of poly(De) (71.7 °C), probably arising from the lower crystallinity caused by the comonomer Cy (Fig. S63 in ESI). However, the T_g s of the resulting copolyesters increased dramatically with the increase of Cy content, –29.1 °C for 60.1 mol% Cy and 3.2 °C for 81.3 mol% Cy, respectively (Table 1, entries 20, 21). This result indicated that aliphatic rings in polymer chain can significantly improve its thermal property. To further enhance the thermal properties of copolymers by adjusting regularity, *trans*-1,4-cyclohexanedimethanol (T-Cy) was subjected to the copolymerization experiments (Table 1, entries 22–24) and high conversions of T-Cy were obtained. As desired, the thermal properties of poly(T-Cy) were improved compared to those derived from the *cis/trans* mixture, meaning that more regular chain structures in the former (Table 1, entries 4 and 5, Fig. S64 in ESI). According to NMR analysis, we could deduce that the carbonyl moieties in poly(De-co-T-Cy) are mainly originated from De, suggesting the profound influence of steric hindrance around the hydroxy groups in the monomers (Fig. S38 in ESI). The steric encumbered monomer Cy is more difficult to convert into the intermediate aldehyde. To explicitly explore the polymerization activities of linear and cyclic monomers, we conducted the kinetic investigation on copolymerization of Cy and De. The samples were taken from the copolymerization system with the monomers feeding ratio of 1:1 at different times, and the relationships between copolymer composition and reaction time are exhibited in Fig. S69 (in ESI). As can be seen, the contents of De and Cy in copolymer increased with reaction time gradually, and the content of De was always slightly higher than that of Cy at any time. This result suggested that De is more reactive than Cy, probably due to the small steric hindrance of De make its hydroxy group easy to approach and coordinate with the central metal to form the intermediate aldehyde.

Choosing poly(De-co-T-Cy) (Table 1, entry 21) as model compound to analyze its sequence structures, we could deduce all the linkage and sequence structures as displayed in Fig. S72 (in ESI). It should be noted that the linkage structure **A₄** generates from the –CH₂OH groups located on the *equatorial* bonds isomerizing to the *axial* bonds in T-Cy and subsequently converting into carbonyl groups during the high temperature polymerization. All characteristic carbons in Fig. S72 (in ESI) can be found in the quantitative ¹³C-NMR spectra of Fig. S73 (in ESI): a is the carbonyl carbon originating from the sequence structure BA₂, which was marked as a↔BA₂ (similarly: b↔A₁A₂, c↔BA₁, d↔A₁A₁, e↔A₄, f↔A₃B/BB). Therefore, the contents of sequence structures in poly(De-co-T-Cy) from BA₂ to A₃B/BB corresponding to a–e are 0.21, 1.03, 0.16, 0.81, 0.90, 1.00 respectively.

We then investigated the copolymerization of De with aromatic monomer Be, which was more rigid than Cy. ¹H-NMR spectrum of the resulting copolymer displayed four sets of characteristic peaks (Figs. S49–S52 in ESI), further suggesting the different ester linkages in the polymer chain. DSC results

showed that the T_m decreased with the increase of Be content in copolymer because of the disrupted crystallinity. Unfortunately, the T_g s were not observed in these two cases, thus no direct evidence could be provided to verify the enhancement of thermal properties.

Chemical recovery of the end-of-life polyesters to original monomers has emerged as an elegant strategy to tackle the energy and environmental problems caused by plastic waste^[40]. However, the existing chemical recycling methods mainly focus on pyrolysis, hydrolysis, chemolysis and so on, which still face challenges such as energy-intensive and incomplete depolymerization. Hydrogenative depolymerization based on transition metal catalysts is a green and sustainable approach for polymer recycling, which has shown powerful capability for depolymerization of PET and nylons.^[39] Therefore, we started to degrade and recycle the as-obtained copolyesters with this method based on Milstein catalyst. Toluene was chosen as the solvent to conduct the catalytic hydrogenation experiment of polyesters because of its good solubility and high boiling point. Under 1.2 MPa H₂ pressure, poly(De-co-Cy) was successfully converted into the pristine monomers by simple heating the reaction system at 120 °C for 48 h. As shown in the ¹H-NMR spectra (Fig. 4), the copolymer derived from the monomer feeding ratio of [De]/[Cy]=5/5 achieved complete depolymerization back to the original two monomers *via* catalytic hydrogenation by the same catalyst as the polymerization. Nevertheless, the molar fraction of *cis/trans* conformation of the recovered monomer has a little change, maybe arising from the conformational isomerism of Cy in the hydrogenation process (Fig. 4c). Furthermore, the contents of recycled monomers were equal to those of two monomers in the copolymer, suggestive of near-quantitative recycling of the polymer. To gain insight into how the monomer structures influence the depolymerization activities, hydrogenative depolymerization of the mixture of poly(De) and poly(Cy) with the feeding molar ratio *ca.* 1:1 for 1 h and 4 h were conducted respectively. As shown in the ¹H-NMR spectra (Fig. S71 in ESI), the recovery rates of De and Cy were 24.0% and 23.6% respectively at 1 h, and which ascended to 93.3% and 92.6% respectively at 4h. These results indicated that depolymerization rate of poly(De) is slightly

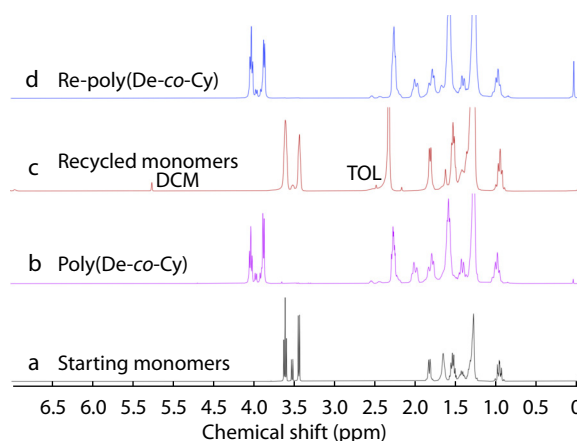


Fig. 4 ¹H-NMR spectra of (a) starting monomers (Cy, De), (b) poly(De-co-Cy) (Table 1, entry 19), (c) recycled monomers from poly(De-co-Cy), (d) reformed poly(De-co-Cy).

higher than that of poly(Cy), consistent well with the polymerization results as above-mentioned. To avoid the use of toxic solvent, we further investigated the hydrogenative depolymerization experiment on copolymers derived from the monomer feeding ratio of [De]/[He]=60/40 under solvent-free conditions (Table S1 in ESI). Excitingly, the recyclability was better than that in toluene. A large amount of white substance was sublimated to the inner wall of the reactor during the reaction process, which was identified by NMR spectroscopy as pure monomers in almost quantitative conversion (Figs. S53, S56 and S57 in ESI).

The biggest advantage of this depolymerization method is that it avoids the costly and time-consuming purification process. The recycled monomers De and Cy were directly repolymerized again in the absence of solvent utilizing the same Ru complex (0.2 mol%) and KO^tBu (0.2 mol%) for 72 h to produce the corresponding copolyester with almost unchanged molecular weight and thermal properties (Fig. 4d). Therefore, dehydrogenative polymerization-hydrogenative depolymerization process has been utilized successfully to establish a closed loop cycle for polyester synthesis and degradation. In

the meanwhile, we also examined the hydrolysis of the copolymer. Under alkaline conditions, the copolymer was mostly hydrolyzed to pristine diols, hydroxy-carboxylates and dicarboxylates, but the poor solubility of water led to incomplete depolymerization and formation of small amounts of oligomers. Adding THF to dissolve the polymer, followed by acidification of the product mixture yielded the original diols, two kinds of hydroxy-acids and two kinds of diacids, as corroborated by NMR analyses (Figs. S67 and S68 in ESI). These different building blocks result in irregular polyester chain structures as aforementioned.

Based on experimental results and recent computational studies,^[41–45] the plausible mechanisms for diols to (co)polyester and its hydrogenative depolymerization are proposed in Fig. 5. For diol (co)polymerization (Fig. 5a): First, the dearomatized species I obtained by deprotonation of the benzylic phosphine “arm” of Milstein catalyst precursor reacts with diols to form the aromatized ruthenium alkoxide II, which is readily converted into dihydride species III and hydroxy-aldehyde *via* β -H elimination. III is considered as the real active species in present system, this is in line with Gusev’s report^[45]

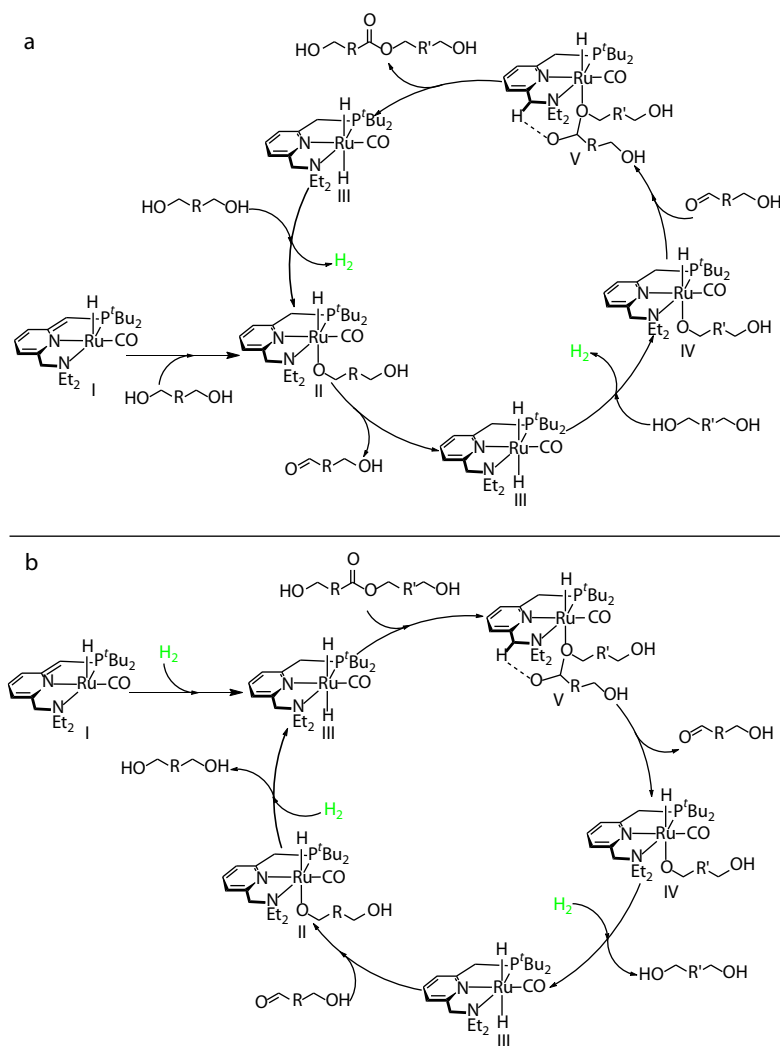


Fig. 5 Proposed dehydrogenative polymerization mechanism of diols (a) and hydrogenative depolymerization mechanism of (co)polyesters (b) catalyzed by Milstein catalyst.

but different from Robertson's report.^[35] Then, III reacts with another diol to form alkoxide IV (if R' = R, IV = II), which undergoes outer-sphere addition with new formed aldehyde moiety to afford hemiacetaloxide species V. Finally, V regenerates dihydride III and gives ester linkage *via* rearrangement and hydride abstraction. III enters directly into the next catalytic cycle and the dearomatized complex I does not need to regenerate again, this is different from the bifunctional double hydrogen transfer (BDHT) mechanism.^[32,46–48] For (co)polyester depolymerization (Fig. 5b): I is firstly aromatized by H₂ to afford dihydride III, one hydride (H⁻) of which attacks the ester group of polyester to form the hemiacetaloxide species V. V is not stable and immediately converts into Ru alkoxide IV, which facilitates the heterolytic splitting of H₂ to produce dihydride species III along with formation of diol. III further attacks the new-formed hydroxyaldehyde to generate alkoxide II, and finally affording another diol by repeating the process of IV to III. As can be seen, in the whole process of circular monomer-polymer-monomer cycle, only H₂ is produced or consumed, thus proving a green and sustainable strategy in this study.

CONCLUSIONS

We have successfully established the circular monomer-polymer-monomer cycle through combination of dehydrogenative polycondensation and hydrogenative depolymerization by utilizing commercially available diols and Milstein catalyst. These green and sustainable methods produce the only by-product H₂ in the polymerization process and it can be reused as the sole additive in the depolymerization process, thus providing an atom-economical closed-loop reaction cycle. Through copolymerization of various diols, a series of aliphatic and aromatic copolyesters with versatile microstructures and properties were obtained. The thermal properties and molecular weight of the copolymers can be tailor-made by incorporation of long-chain or ring-containing diols and adjusting the feeding ratio of two monomers. It is worth noting that the *T_m* of the homopolyester is lower than that of its counterpart derived from ROP of cyclic lactone, probably ascribing to the regioirregular ester linkages in present system. More strikingly, the (de)polymerization can be conducted in solvent-free condition and the recycled monomers can be used directly because of their high purities, exhibiting the potential industrial applications. Further extension of monomer scopes to prepare high-performance chemically recyclable polyesters and development of new catalysts to realize the regioselective (co)polymerization of diols are ongoing in our laboratories.

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/s10118-023-2903-9>.

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