Polymer Chemistry

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Cite this: *Polym. Chem.*, 2023, **14**, 1019

An efficient cyclodepolymerization route for the chemical recycling of poly(ethylene adipate)†

Hongjuan Li,‡[a,c] Xiangxiang Yan,‡[b] Jie Huan,[b] Sheng Wang,[b] Xiaohong Li,[b] Yatao Wang,[c] Yingfeng Tu *[b] and Zhiping Li *[a]

Received 31st December 2022,
Accepted 29th January 2023

DOI: 10.1039/d2py01613c

rsc.li/polymers

Cyclodepolymerization is a special chemical recycling (upcycling) method for polyesters based on ring–chain equilibria in solution, yet it is usually carried out in halogenated solvents at temperatures around 200 °C. We present here a green cyclodepolymerization route for the efficient chemical recycling of poly(ethylene adipate) (PEA) to its cyclic oligomers, cyclic oligo(ethylene adipate)s (COEAs), using dibutyltin oxide as a catalyst and toluene as a solvent. The effect of solvent on the COEAs yield was studied, and toluene was found to be a better solvent than chlorobenzene since it provides higher yields in addition to the facile purification of COEAs from the reaction mixture due to the solubility difference between PEA and COEAs. The effects of PEA concentration, reaction time and catalyst amount on the yield of COEAs are thoroughly studied. Our results show that the yield of COEAs increases with reduced PEA concentration, prolonged reaction time and increase of catalyst amount. Since COEAs are readily polymerized to pristine PEA, our strategy affords a closed-loop chemical recycling way of PEA.

Introduction

Poly(ethylene adipate) (PEA) is a well-known crystalline aliphatic polyester with applications as plasticizers and as precursors for the synthesis of polyurethanes.[1–5] With the dramatic increase of polyurethane production, which reached around 28 million tons in 2020,[6] the annual production of PEA is now ranked the largest among aliphatic polyesters. Since aliphatic polyesters are considered as biodegradable materials, they are usually discarded directly into the environment. Yet their degradation is very slow in sea water or under conventional waste management conditions like landfill.[7–14] In addition, the environmental issues caused by small molecular byproducts during degradation are not clear. Thus, it is of great significance to study the chemical recycling of PEA for sustainable development through material regeneration. However, to our knowledge, the chemical recycling (upcycling) of PEA has not been reported.

Hydrolysis, alcoholysis (glycolysis), and aminolysis are traditional chemical recycling strategies for aromatic polyesters.[15–27] Due to the high energy cost and waste treatment during the recycling process, the obtained products/monomers are quite expensive compared to their petroleum-based counterparts. The cyclodepolymerization method can be considered as a fourth way for the chemical recycling of polyesters and polycarbonates, although it is much less studied, where polyesters are converted to corresponding cyclic oligoesters based on ring–chain equilibria in dilute solutions.[28–37] The obtained cyclic oligoesters can be used as monomers for ring-opening polymerization (ROP), yielding high molecular weight polyesters that cannot to be synthesized by typical condensation polymerization.[38–46] Recently, we developed a cascade polycondensation-coupling ring-opening polymerization (PROP) method, where high molecular weight polyesters with high functional group content can be synthesized *via* the polymerization of cyclic oligoesters with functional diols, greatly extending the applications of cyclic oligoesters and polyesters.[47–51] Although cyclic monomers can be synthesized by the pseudo-high dilution cyclization (PHDC) of diacyl chlorides with diols, their yields are quite low (20–40%) with large amounts of solvents used.[52–55] Thus, the cyclodepolymerization method provides an efficient and low-cost method for the preparation of high-value added cyclic monomers, and shows great advantages among chemical recycling methods.

Despite the potential benefits from the cyclodepolymerization strategy in the chemical recycling of aromatic polyesters, it must be carried out at high temperatures (~180 °C) in high boiling point toxic solvents like dichlorobenzene due to solubility problems, with a long reaction time (typically a few days),

---

[a] *Department of Chemistry, Renmin University of China, Beijing 100872, China. E-mail: zhipingli@ruc.edu.cn*
[b] *College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China. E-mail: tuyingfeng@suda.edu.cn*
[c] *Coal Chemical R&D Center, Kailuan Group, Tangshan, Hebei 063611, China*

† Electronic supplementary information (ESI) available: Materials, instrumentation, experimental details, ^{1}H NMR results and SEC curves. See DOI: **https://doi.org/10.1039/d2py01613c**

‡ These authors contributed equally to this work.

severely limiting its applications.[28–34] In this work, we would like to investigate the chemical recycling of PEA to its cyclic oligomers, cyclic oligo(ethylene adipate)s (COEAs), using dibutyltin oxide as a catalyst, as shown in Scheme 1a. The solution cyclodepolymerization of PEA in dichlorobenzene was studied first to testify if the strategy works. Since aliphatic polyesters and the corresponding cyclic oligoesters have much better solubility than their aromatic counterparts, and while toluene is a good solvent for COEAs but a non-solvent for PEA at room temperature, an energy-saving chemical recycling method for PEA was established by carrying out the cyclodepolymerization reaction in toluene under mild reaction conditions, with a facile purification process utilizing their solubility difference. The effects of concentration, reaction time and catalyst amount on the yield of COEAs have been systematically studied. Finally, the obtained COEAs were polymerized to PEA diols to test the closed-loop chemical recycling of PEA.

Experimental section

Synthesis of COEAs *via* the PHDC method

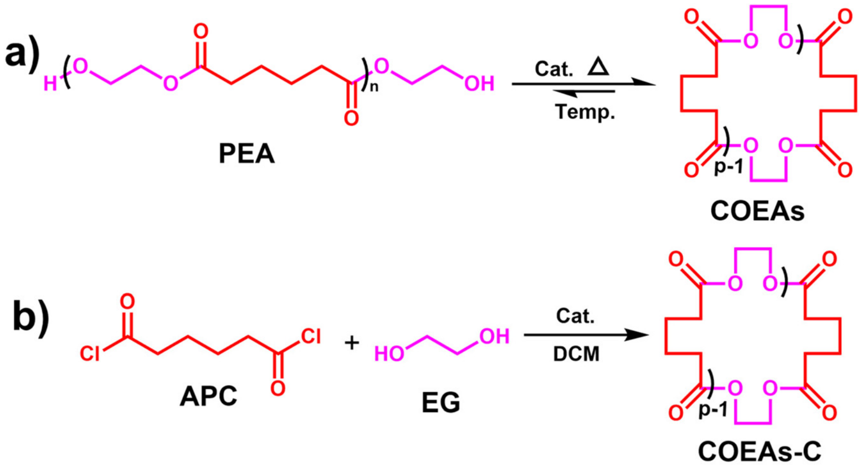
COEA control samples were synthesized by the cyclization of adipoyl chloride and ethylene glycol under pseudo-high dilution conditions, as shown in Scheme 1b.[53] A 500 mL three-necked flask with a magnetic stirrer and a nitrogen inlet, was charged with a solution of pyridine (1.90 g) in 200 mL of dichloromethane (CH_2Cl_2). The solution was set to 40 °C, and a solution of adipoyl chloride (2.01 g) and ethylene glycol (0.62 g) in a CH_2Cl_2/THF mixture (10 mL/10 mL) was added slowly over 1.5 h. The reaction was quenched with ammonium hydroxide (5 mL), filtered, and the organic layer was washed with dilute hydrochloric acid (1 M) and then deionized water three times, and dried over sodium sulphate. After filtration, the crude product was obtained by the removal of the solvent. Pure COEAs were obtained by column chromatography (eluent: 4% acetone in dichloromethane). The product was dried under vacuum at room temperature for 12 h and denoted as COEAs-C. Yield: 31%. MALDI-TOF mass: $[\text{2-mer} + Na]^+$ ($C_{16}H_{24}O_8Na^+$, m/z theoretical value: 367.37, detected: 367.01), $[\text{3-mer} + Na]^+$ ($C_{24}H_{36}O_{12}Na^+$, m/z theoretical value: 539.56, detected: 539.30).

Synthesis of COEAs *via* cyclodepolymerization

PEA solutions in toluene (10 g L^{-1} to 100 g L^{-1}) were heated at reflux temperature and reacted for different times (3–120 h) in the presence of dibutyltin oxide (0.5–4 wt% to the PEA amount). The reaction was finished by cooling to room temperature and then refrigerated (~4 °C). After filtration, the organic layer was washed three times with diluted HCl, and then deionized water and dried. The solvent was removed by vacuum evaporation, and COEAs were obtained after vacuum drying without further purification. Yield: 8–99%. MALDI-TOF mass: $[\text{2-mer} + Na]^+$ ($C_{16}H_{24}O_8Na^+$, m/z theoretical value: 367.37, detected: 367.29), $[\text{3-mer} + Na]^+$ ($C_{24}H_{36}O_{12}Na^+$, m/z theoretical value: 539.56, detected: 539.27), $[\text{4-mer} + Na]^+$ ($C_{32}H_{48}O_{16}Na^+$, m/z theoretical value: 711.76, detected: 711.32), $[\text{5-mer} + Na]^+$ ($C_{40}H_{60}O_{20}Na^+$, m/z theoretical value: 883.95, detected: 883.40), $[\text{6-mer} + Na]^+$ ($C_{48}H_{72}O_{24}Na^+$, m/z theoretical value: 1056.14, detected: 1055.48), $[\text{7-mer} + Na]^+$ ($C_{56}H_{84}O_{28}Na^+$, m/z theoretical value: 1228.33, detected: 1227.57), $[\text{8-mer} + Na]^+$ ($C_{64}H_{96}O_{32}Na^+$, m/z theoretical value: 1400.53, detected: 1399.66), $[\text{9-mer} + Na]^+$ ($C_{72}H_{108}O_{36}Na^+$, m/z theoretical value: 1572.72, detected: 1571.74), $[\text{10-mer} + Na]^+$ ($C_{80}H_{120}O_{40}Na^+$, m/z theoretical value: 1748.32, detected: 1748.51).

Synthesis of PEA *via* PROP

COEAs and 1,10-decanediol with a weight ratio of 5/1 were charged to a three-necked flask with a mechanical stirrer and a nitrogen inlet. The reaction mixture was heated to 230 °C for 5 min under a nitrogen atmosphere, and then $Ti(n\text{-}C_4H_9O)_4$ (0.05 wt%) was charged to start the polymerization. The mixture was polymerized for 120 min, and subsequently quenched by cooling to room temperature. The obtained



Scheme 1 Synthetic route to cyclic oligo(ethylene adipate)s (COEAs) *via* a cyclodepolymerization (CDP) method (a) and a pseudo-high dilution cyclization method (b).

product was subjected to gel permeation chromatography (GPC) measurement without further purification.

Results and discussion

Solubility of PEA and COEAs

The cyclodepolymerization of polyesters in a diluted solution based on ring–chain equilibria has been well-established for the preparation of aromatic cyclic oligoesters. In the presence of a suitable catalyst, equilibria can be established between polyester linear chains and their corresponding cyclic oligomers.[28–30] The equilibria depends greatly on the concentration, and previous reports revealed that at dilute concentrations (<3% w/v), cyclic oligoesters are the main products.[33,34] As the cyclodepolymerization of aromatic polyesters is usually carried out in toxic chlorobenzene or dichlorobenzene solvents at elevated temperatures due to solubility problems, a less toxic solvent for the cyclodepolymerization of PEA is preferred since it has much better solubility than its aromatic counterparts. In addition, considering that cyclic oligomers typically exhibit better solubility than their corresponding linear polymers, we would like to find a solvent in which COEAs and PEA have a large solubility difference at room temperature, thus the purification would be made quite easy just by filtration.

For property investigations, controlled COEA samples (COEAs-C) were synthesized under pseudo-high dilution conditions, as shown in Scheme 1b. The MALDI-TOF MS spectrum of COEAs-C is presented in Fig. 1a. The peaks match well with the mass of sodium-cationized cyclic oligoesters, where the peak at 367.01 (*m*/*z*) can be assigned to the cyclic dimer (C2EA) ($C_{16}H_{24}O_8Na^+$, theoretical value: 367.37), while that at 539.30 to the cyclic trimer (C3EA) ($C_{24}H_{36}O_{12}Na^+$, theoretical value: 539.56). Interestingly, there are no cyclic oligoesters with a higher degree of oligomerization observed, suggesting that the dimer and trimer are more kinetically favored. No linear oligoester is observed, indicating the high purity of cyclic oligoesters.

Fig. 1b shows the GPC curve of COEAs-C. Only two distinguished peaks are observed, consistent with the results from MALDI-TOF mass spectrometry experiments. The peak at retention volumes of 22.9 mL and 24.0 mL can be assigned to C3EA and C2EA, respectively. The weight fraction of cyclic oligomers can be roughly estimated by the corresponding peak areas. The contents of dimer and trimer are around 89% and 11%, respectively.

Fig. 2 shows the ^{13}C NMR spectra of COEAs-C and PEA, with the peak assignments presented in the figure insets. COEAs and PEA exhibit similar ^{13}C NMR spectra. The peaks at chemical shifts of around 24.2 ppm (peak a,

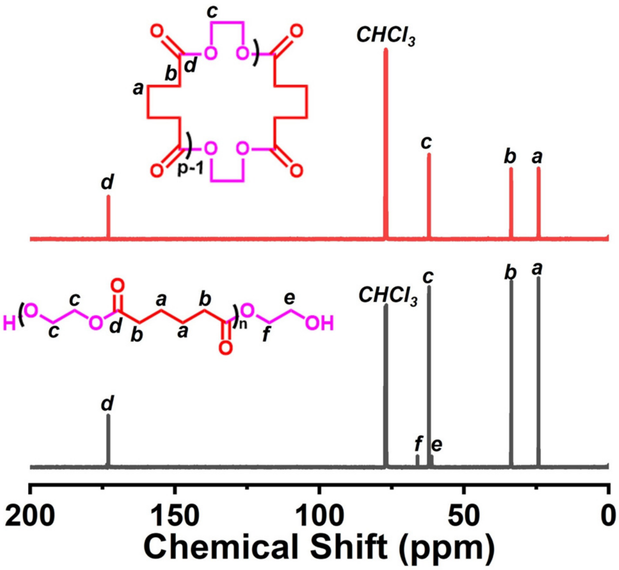


Fig. 2 ^{13}C NMR spectra of COEAs-C and PEA.

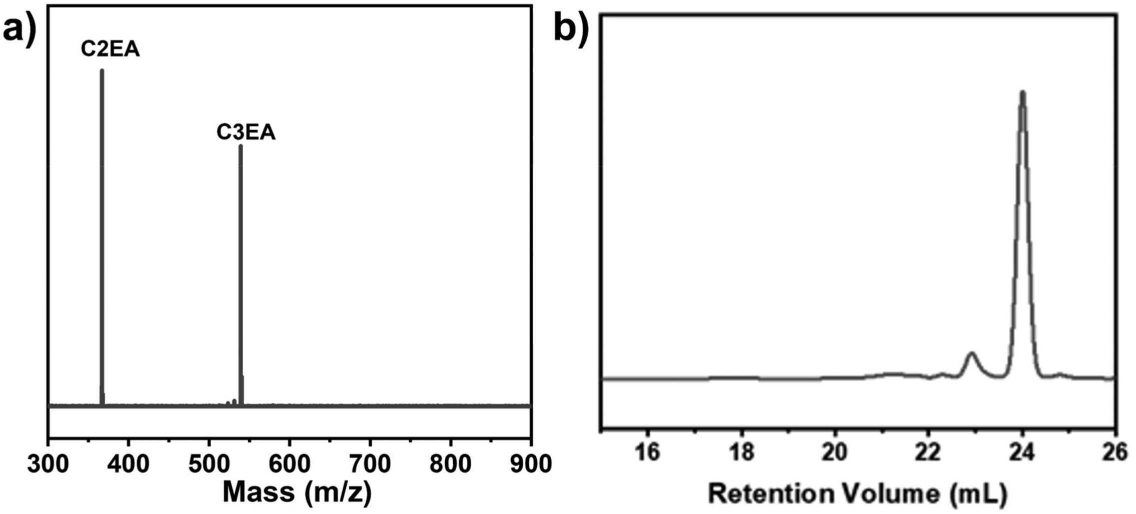


Fig. 1 MALDI-TOF mass spectrum (a) and GPC curve (b) of COEAs-C.

$\text{OOCCH}_2\mathit{CH}_2\mathit{CH}_2\text{CH}_2\text{COO}$), 33.7 ppm (peak b, $\text{OOC}\mathit{CH}_2\text{CH}_2\text{CH}_2\mathit{CH}_2\text{COO}$) and 172.9 ppm (peak d, *C*OO) are assigned to the carbon atoms from adipic acid segments. The peaks at 62.1 ppm (peak c, $\text{O}\mathit{CH}_2\mathit{CH}_2\text{O}$) are assigned to the carbon atoms from ethylene glycol segments, respectively. For PEA, two additional peaks at 61.1 ppm (peak e, $\text{OCH}_2\mathit{CH}_2\text{OH}$) and 66.1 ppm (peak f, $\text{O}\mathit{CH}_2\text{CH}_2\text{OH}$) were observed, ascribed to the chain-end groups, which are absent in COEAs. Similar results were also observed in their ^{1}H NMR spectra (Fig. S1†), where the chain-ends for PEA are detected while COEAs-C show no chain-ends. The above characterization results confirm the successful synthesis of COEAs-C with high purity.

PEA was synthesized *via* traditional condensation polymerization as shown in Scheme S1.† In this study, PEA with a number-average molecular weight (M_n) of 9860 g mol^{-1} and a polydispersity ($Đ$) of 1.97 was used as a raw material for the synthesis of COEAs *via* cyclodepolymerization, with its GPC curve presented in Fig. S2.† Quite interestingly, besides the major peak at a retention volume of 17.0–21.0 mL, there are a few weaker peaks observed at a retention volume of 21.7–25.0 mL. By comparison with the curve of COEAs-C, these peaks can be ascribed to COEAs with different ring sizes, formed as the thermodynamic ring–chain equilibrium products during condensation polymerization. The COEA content is a few percentages, calculated from the peak area ratio. This is consistent with the typical results during bulk condensation polymerization of aromatic polyesters, where there are about 1–3% cyclic oligoesters coexisting with linear polyesters.[42,55]

Using COEAs-C as a controlled sample, its solubility in different solvents was tested in addition to that of PEA. The results are summarized in Table 1. It shows that COEAs-C have very good solubility in most common solvents at room temperature except alkanes. For PEA, it has good solubility in polar solvents like dichlorobenzene, DMF and dioxane, but limited solubility in non-polar solvents like toluene and alkanes. When heated to around 100 °C, the solubility increased greatly and PEA can be dissolved in toluene. Solubility tests in alcohols and esters were not performed as these solvents may react with PEA *via* the transesterification mechanism under cyclodepolymerization conditions.

Cyclodepolymerization of PEA

Since PEA and COEAs have good solubility in DCB and chlorobenzene (CB), the cyclodepolymerization of PEA in these solvents was carried out with the results summarized in Table 2. The concentration was fixed at 25 g L^{-1}, using 3% $\text{SnO(C}_4\text{H}_9\text{)}_2$ (*vs.* PEA amount) as catalyst, similar to the reaction conditions reported for the cyclodepolymerization of aromatic polyesters.[28–30] Preliminarily studies show that cyclodepolymerization proceeded well in DCB and CB, with the yield ranging between 35 and 70% (trials 1 to 5). The reaction carried out in CB provided a better yield than it did in DCB, despite the temperature (130 °C) being much lower than that in DCB (~180 °C) (trial 1 *vs.* 3); the latter is the traditional cyclodepolymerization temperature used for aromatic polyesters. As the ring–chain equilibrium is based on the transes-

Table 1 Solubility of PEA and COEAs in different solvents

Sample	DCB	CB	Toluene	DMF	Xylene	THF	CHCl_3	Decane
COEAs[a]	++	++	++	++	++	++	++	−−
PEA[a]	++	++	−−	++	−−	+	++	−−
PEA[b]	++	++	++	++	+	N.A.	N.A.	+

[a] At room temperature. [b] At 80 °C. ++: >200 g L^{-1}, −−: <0.1 g L^{-1}, +: ~100 g L^{-1}, N.A.: not applicable.

Table 2 The yield of COEAs under various cyclodepolymerization conditions

Entry	Solvent	*T* (°C)	Time (h)	Concentration (g L^{-1})	Catalyst	Yield (%)
1	DCB	180	24	25	3%	45
2	CB	130	6	25	3%	35
3	CB	130	24	25	3%	48
4	CB	130	72	25	3%	59
5	CB	130	120	25	3%	67
6	Tol	110	6	25	3%	24
7	Tol	110	12	25	3%	56
8	Tol	110	24	25	3%	59
9	Tol	110	48	25	3%	89
10	Tol	110	96	25	3%	~99
11	Tol	110	24	10	3%	88
12	Tol	110	24	17	3%	79
13	Tol	110	24	50	3%	33
14	Tol	110	24	100	3%	30
15	Tol	110	24	25	0.5%	8
16	Tol	110	24	25	1%	21
17	Tol	110	24	25	2%	30
18	Tol	110	24	25	4%	67

terification between the ester bonds of PEA and COEAs, this suggests that the activation energy for aliphatic polyesters is lower than that for aromatic polyesters, probably due to the reduced steric hindrance from aliphatic chains. Thus, the cyclodepolymerization of PEA can be carried out at much lower temperatures, which facilitates the utilization of less toxic solvents with a low boiling point.

The effect of reaction time on the yield of COEAs in CB was studied, and the results are plotted in Fig. 3. The yield increases with prolonged reaction time, but the increment rate slows down after 72 h. This suggests that the ring–chain thermodynamic equilibrium state may be achieved under such reaction conditions, with the yield of COEAs at around 60%.

As PEA can be dissolved well in toluene at around 100 °C, but precipitates out after cooling to room temperature, while COEAs are well dissolved in toluene even at refrigerated temperature, we anticipate that the cyclodepolymerization of PEA in toluene has many merits if it works, as the purification process will be greatly shortened and energy cost reduced just by cooling down the solution to room temperature or lower. The unreacted PEA will precipitate from the solution, and pure COEAs can be obtained after filtration, washing and removal of the solvent. Subsequently, the cyclodepolymerization of PEA in toluene was carried out at reflux temperature, and the post-reaction solution was treated following the above protocol.

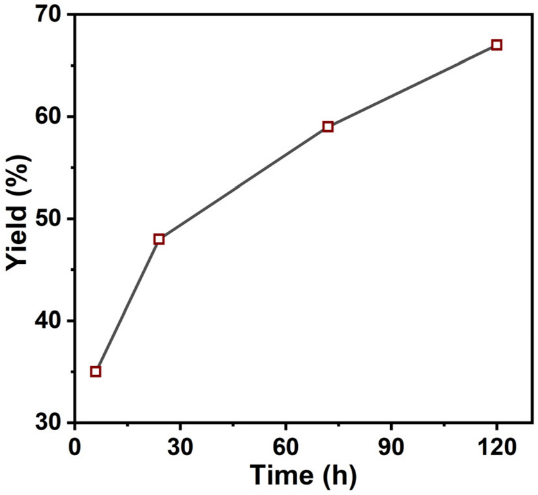


Fig. 3 The yield of COEAs as a function of the cyclodepolymerization time of PEA in chlorobenzene.

Fig. 4a shows the MALDI-TOF mass spectrum of COEAs after the cyclodepolymerization of PEA in toluene for 24 h at reflux temperature (trial 8). Unlike the COEAs-C sample, COEAs with different ring sizes are observed, from the dimer (C2EA) to the nonamer (C9EA). Among these, the tetramer (C4EA) shows the highest peak intensity. This indicates that the solution depolymerization of PEA in toluene works with the ring–chain equilibrium, although the reaction temperature is much lower than that for aromatic polyesters. Moreover, there is no linear PEA observed, suggesting that the purification protocol works well here.

Fig. 4b shows the GPC curve of the obtained COEAs from trial 8. By comparison with the curves of COEAs-C, the peak assignment is annotated at the peak top. Distinct peaks from the dimer (C2EA) to the pentamer (C5EA) are observed, with those products at a lower retention volume being a mixture of cyclic oligomers with a higher degree of oligomerization. However, differing from the MALDI-TOF mass spectrum, the GPC result shows that C2EA is the largest portion present among the products estimated from the peak area. This is reasonable as the MALDI-TOF mass spectrometry technique is not sensitive to very low molecular weight products.

The effects of concentration, catalyst amount and reaction time on the COEA yield were studied, and the results are provided in Table 2. Fig. 5 shows the effect of reaction time on the yield of COEAs. The yield increases with a prolonged reaction

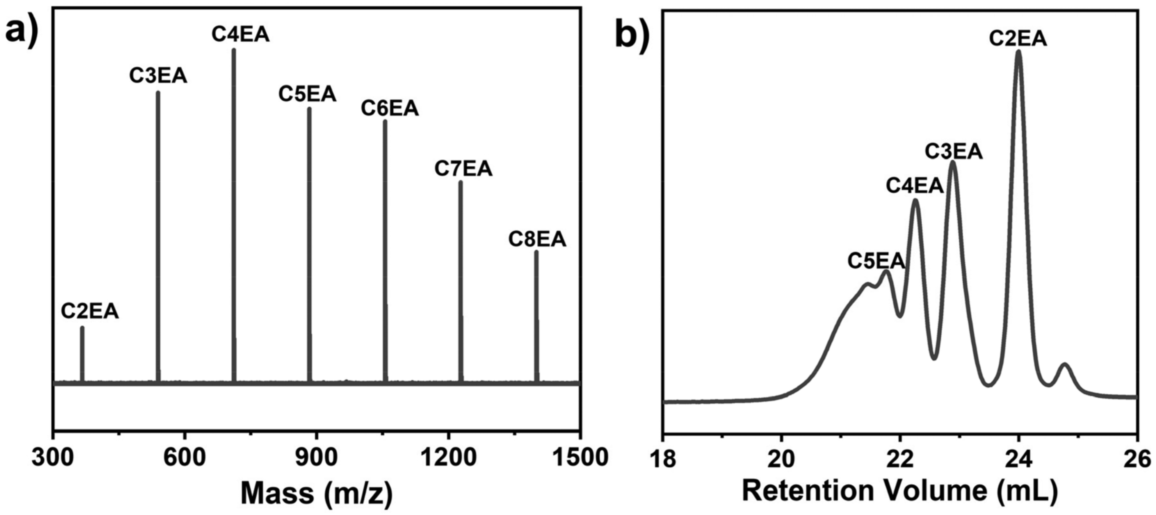


Fig. 4 MALDI-TOF mass spectrum (a) and GPC curve (b) of COEAs obtained from trial 8 after purification.

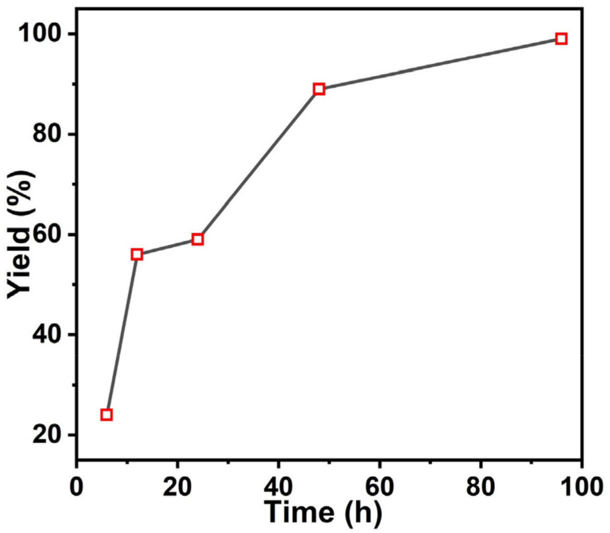


Fig. 5 The yield of COEAs as a function of the PEA cyclodepolymerization time in toluene. Conditions: PEA initial concentration of 25 g L^{-1}, 3% $SnO(C_4H_9)_2$.

time, and reaches ~99% after 4 days of depolymerization. When compared to chlorobenzene, the reactions carried out in toluene provide higher yields. This suggests that the solvent also has a significant effect on the ring–chain equilibrium. In addition, at lower reaction temperatures, side reactions like oxidation will be greatly suppressed, thus a higher product yield is obtained. Using toluene instead of chlorobenzene greatly increases the yield of COEAs, with 90% or higher being achieved after a long reaction time.

Fig. 6 shows the effect of the starting PEA concentration on the yield of COEAs. The yield increases by lowering the PEA concentration. This is consistent with Jacobson and Stockmayer's theory of ring–chain equilibria,[56] where the yield decreases with an increase of concentration. However, the reaction efficiency will be reduced at lower concentrations since a large quantity of solvents should be used and their removal will require a lot of energy.

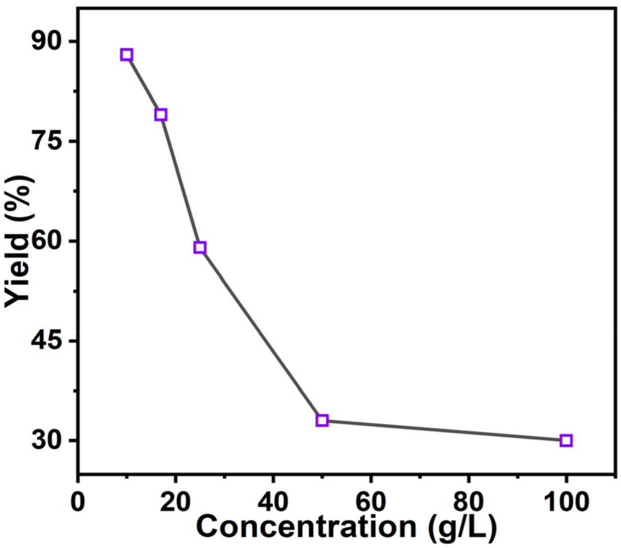


Fig. 6 The yield of COEAs as a function of the initial concentration of PEA in toluene. Conditions: 24 h cyclodepolymerization time, 3% $SnO(C_4H_9)_2$.

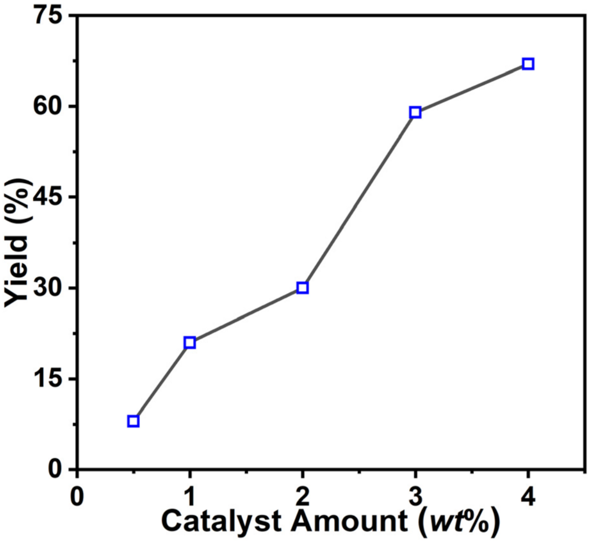


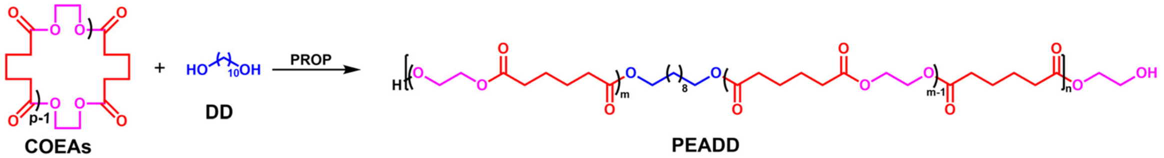
Fig. 7 The yield of COEAs as a function of the catalyst amount (relative to PEA) in toluene. Conditions: 24 h cyclodepolymerization time, PEA initial concentration of 25 g L^{-1}.

Fig. 7 shows the effect of catalyst amount on the yield of COEAs. Roughly, the yield increases linearly with an increase of $SnO(C_4H_9)_2$ catalyst concentration. This suggests that dibutyltin oxide effectively promotes ring–chain equilibria and the formation of cyclic products. Although an increase in the catalyst amount will enhance the depolymerization speed of PEA and increase the yield of COEAs, it also increases the cost since the catalyst is more expensive than PEA. In addition, the removal of $SnO(C_4H_9)_2$ may be a problem when its concentration is high, and its contamination in COEAs may affect their polymerization to PEA-based copolymers.

Synthesis of PEA using COEAs

To test whether the obtained COEAs could be used as monomers for the synthesis of PEA, COEAs and 1,10-decanediol (weight ratio 5 : 1) were mixed together and their melt polymerization was carried out following the PROP method, as shown in Scheme 2. Fig. S3† shows the GPC curves of the resultant PEA. After the polymerization, a single peak at a much lower retention volume compared to COEAs is observed. The estimated M_n and $Đ$ of the resultant PEA are 22.2 kg mol^{-1} and 1.82, respectively, indicating the successful synthesis of PEA. The peaks for COEAs are nearly diminished, showing the high conversion of COEAs.

The thermal properties of raw PEA synthesized by CP and used for cyclodepolymerization studies (PEA-CP), and the chemically recycled PEA synthesized by PROP (PEA-PROP) were



Scheme 2 Synthetic route to PEA using COEAs and *via* a polycondensation-coupling ring-opening polymerization (PROP) method.

studied. Fig. S4† shows the TGA curves of PEA-CP and PEA-PROP, where a single weight loss stage is observed for both samples. The 5% weight loss temperature (T_d) under nitrogen is at 282 °C for PEA-CP, and 315 °C for PEA-PROP, respectively. The PEA sample from chemical recycling shows better thermal stability, probably due to the better thermal stability from 1,10-decylene adipate (DA) segments in the polyester main chain.

Fig. S5† shows the DSC curves of raw PEA and chemically recycled PEA. The melting temperature (T_m) of PEA-CP detected (47 °C) is much higher than that of PEA-PROP (33 °C). This is due to the incorporation of DA segments in PEA chains, which act like defects and thus decrease the crystal melting temperature. The crystallization temperature (T_c) detected under cooling is much less affected (8 °C for PEA-CP and 7 °C for PEA-PROP, respectively), as it is more kinetically controlled.

Conclusions

We have established a special chemical recycling method by the cyclodepolymerization of PEA in toluene solution to its cyclic oligomers following ring–chain equilibria. Our results show that in differing from their aromatic counterparts, aliphatic polyesters can be converted to their cyclic oligoesters under mild conditions in the presence of a tin catalyst. The yield of COEAs increases with increasing reaction time and catalyst amount, and by decreasing the initial concentration of PEA. The obtained COEAs can be polymerized to PEA, providing chemical closed-loop recycling of PEA. This strategy should work for other aliphatic polyesters, and would greatly improve the sustainable development of polymers.

Author contributions

Y. T. and Z. L. conceived the idea and designed the experiments. H. L., X. Y. and J. H. performed the experiments. X. L. performed the NMR experiments. All the authors analyzed the data and co-wrote the manuscript.

Conflicts of interest

The authors declare the following competing financial interest (s): H. L., J. H., Y. W. and Y. T. are inventors on a Chinese patent related to this work filed by the Soochow University and Kailuan Group (No. 202111289134.6, filed on 2 Nov. 2021). All other authors declare no competing interests.

Acknowledgements

This research work was supported by the National Natural Science Foundation of China (Grant No. 22231008 and 22071167) and the Science and Technology Innovation Program Fund of the Kailuan Group.

References

1 Z. S. Petrovic and J. Ferguson, *Prog. Polym. Sci.*, 1991, **16**, 695–836.
2 J. J. Yang, P. J. Pan, T. Dong and Y. Inoue, *Polymer*, 2010, **51**, 807–815.
3 R. Liang, Y. C. Chen, C. Q. Zhang, J. Ying, X. L. Liu, L. K. Wang, R. Kong, X. Feng and J. J. Yang, *Chin. J. Polym. Sci.*, 2017, **35**, 558–568.
4 J. J. Tang, L. L. Li, X. M. Wang, J. J. Yang, X. Q. Liang, Y. Q. Li, H. M. Ma, S. S. Zhou and J. S. Wang, *Polym. Test.*, 2020, **81**, 106116.
5 S. Nagarajan, C. H. Su and E. M. Woo, *Polymer*, 2022, **257**, 125264.
6 P. Zahedifar, L. Pazdur, C. M. L. Vande Velde and P. Billen, *Sustainability*, 2021, **13**, 3583.
7 A. R. Bagheri, C. Laforsch, A. Greiner and S. Agarwal, *Global Challenges*, 2017, **1**, 1700048.
8 A. Nakayama, N. Yamano and N. Kawasaki, *Polym. Degrad. Stab.*, 2019, **166**, 290–299.
9 F. V. Ferreira, L. S. Cividanes, R. F. Gouveia and L. M. F. Lona, *Polym. Eng. Sci.*, 2019, **59**, E7–E15.
10 Y. H. Xu, F. Y. Zhou, D. M. Zhou, J. T. Mo, H. W. Hu, L. M. Lin, J. S. Wu, M. G. Yu, M. Zhang and H. Chen, *J. Biobased Mater. Bioenergy*, 2020, **14**, 155–168.
11 G. X. Wang, D. Huang, J. H. Ji, C. Völker and F. R. Wurm, *Adv. Sci.*, 2021, **8**, 2001121.
12 L. Zahir, T. Kida, R. Tanaka, Y. Nakayama, T. Shiono, N. Kawasaki, N. Yamano and A. Nakayama, *Polym. Degrad. Stab.*, 2021, **184**, 109467.
13 T. Y. Liu, D. Huang, P. Y. Xu, B. Lu, G. X. Wang, Z. C. Zhen and J. H. Ji, *ACS Sustainable Chem. Eng.*, 2022, **10**, 3191–3202.
14 B. Liu, T. H. Guan, G. Wu, Y. Fu and Y. X. Weng, *Polymers*, 2022, **14**, 1515.

15 M. Ghaemy and K. Mossaddegh, *Polym. Degrad. Stab.*, 2005, **90**, 570–576.

16 V. Sinha, M. R. Patel and J. V. Patel, *J. Polym. Environ.*, 2010, **18**, 8–25.

17 V. Sharma, P. Shrivastava and D. D. Agarwal, *J. Polym. Res.*, 2015, **22**, 241.

18 B. Geyer, G. Lorenz and A. Kandelbauer, *eXPRESS Polym. Lett.*, 2016, **10**, 559–586.

19 L. N. T. Ho, D. M. Ngo, J. Cho and H. M. Jung, *Polym. Degrad. Stab.*, 2018, **155**, 15–21.

20 F. Kawai, T. Kawabata and M. Oda, *Appl. Microbiol. Biotechnol.*, 2019, **103**, 4253–4268.

21 M. Dębowski, A. Iuliano, A. Plichta, S. Kowalczyk and Z. Florjańczyk, *Polimery*, 2019, **64**, 764–776.

22 V. Tournler, C. M. Topham, A. Gilles, B. David, C. Folgoas, *et al.*, *Nature*, 2020, **580**, 216–219.

23 A. Singh, S. L. Banerjee, K. Kumari and P. P. Kundu, *Environ. Sci.*, 2021, **58**, 1–28.

24 X. Chen, Y. D. Wang and L. Zhang, *ChemSusChem*, 2021, **14**, 4137–4151.

25 S. Kaiho, A. A. R. Hmayed, K. R. D. Chiaie, J. C. Worch and A. P. Dove, *Macromolecules*, 2022, **55**, 10628–10639.

26 R. L. Yang, G. Q. Xu, B. Z. Dong, H. B. Hou and Q. G. Wang, *Macromolecules*, 2022, **55**, 1726–1735.

27 J. V. Valh, D. Stopar, I. S. Berodia, A. Erjavec and O. Šauperl, *Polymers*, 2022, **14**, 3244.

28 D. J. Brunelle, G. Kailasam, J. A. Serth-Guzzo and P. R. Wilson, *US* 5668186, 1997.

29 S. C. Hamilton, J. A. Semlyen and D. M. Haddleton, *Polymer*, 1998, **39**, 3241–3252.

30 J. H. Youk, R. P. Kambour and W. J. MacKnight, *Macromolecules*, 2000, **33**, 3606–3610.

31 P. Monvisade and P. Loungvanidprapa, *J. Polym. Res.*, 2008, **15**, 381–387.

32 N. González-Vidal, A. M. de Ilarduya and S. Muñoz-Guerra, *Eur. Polym. J.*, 2010, **46**, 792–803.

33 P. Hodge, *Chem. Rev.*, 2014, **114**, 2278–2312.

34 P. Hodge, *React. Funct. Polym.*, 2014, **80**, 21–32.

35 J. C. Morales-Huerta, A. M. de Ilarduya and S. Muñoz-Guerra, *Polymer*, 2016, **87**, 148–158.

36 P. Fleckenstein, J. G. Rosenboom, G. Storti and M. Morbidelli, *Macromol. React. Eng.*, 2018, **12**, 1800018.

37 W. Zhang, J. Dai, Y. C. Wu, J. X. Chen, S. Y. Shan, Z. Cai and J. B. Zhu, *ACS Macro Lett.*, 2022, **11**, 173–178.

38 J. H. Youk, R. P. Kambour and W. J. MacKnight, *Macromolecules*, 2000, **33**, 3594–3599.

39 P. Monvisade and P. Loungvanidprapa, *Eur. Polym. J.*, 2007, **43**, 3408–3414.

40 P. Siriphannon and P. Monvisade, *Bull. Mater. Sci.*, 2013, **36**, 121–128.

41 I. Flores, A. M. de Ilarduya, H. Sardon, A. J. Müller and S. Muñoz-Guerra, *ACS Appl. Polym. Mater.*, 2019, **1**, 321–325.

42 A. M. D. Ilarduya and S. M. Guerra, *Polym. Chem.*, 2020, **11**, 4850–4860.

43 H. J. Li, S. Y. Xu, J. Li, Y. Y. Tu, X. H. Li, Y. F. Tu, J. H. Li, Y. T. Wang and Z. P. Li, *Polym. Chem.*, 2021, **12**, 1837.

44 J. Huan, J. Li, Y. J. Lan, S. Wang, X. H. Li, X. M. Yang, H. J. Lu and Y. F. T, *Polymer*, 2022, **260**, 125369.

45 J. Bruckmoser, S. Remke and B. Rieger, *ACS Macro Lett.*, 2022, **11**, 1162–1166.

46 G. Q. Xu and Q. G. Wang, *Green Chem.*, 2022, **24**, 2321–2346.

47 Q. Z. Xu, J. Y. Chen, W. C. Huang, T. G. Qu, X. H. Li, Y. W. Li, X. M. Yang and Y. F. Tu, *Macromolecules*, 2013, **46**, 7274–7281.

48 X. Zhu, J. L. Gu, X. H. Li, X. M. Yang, L. Wang, Y. J. Li, H. Li and Y. F. Tu, *Polym. Chem.*, 2017, **8**, 1953–1962.

49 Y. F. Tu, *Acta. Polym. Sin.*, 2019, **50**, 1146–1155.

50 J. Li, Y. Y. Tu, H. J. Lu, X. H. Li, X. M. Yang and Y. F. Tu, *Polymer*, 2021, **237**, 124313.

51 X. T. Wan, J. Jiang, Y. Y. Tu, S. Y. Xu, J. Li, H. J. Lu, Z. K. Li, L. H. Xiong, X. H. Li, Y. L. Zhao and Y. F. Tu, *Polym. Chem.*, 2021, **12**, 6022–6029.

52 D. J. Brunelle, J. E. Bradt, J. Serth-Guzzo, T. Takekoshi, T. L. Evans, E. J. Pearce and P. R. Wilson, *Macromolecules*, 1998, **31**, 4782–4790.

53 M. Lu, X. Zhu, X. H. Li, X. M. Yang and Y. F. Tu, *Chin. J. Polym. Sci.*, 2017, **35**, 1051–1060.

54 Y. Xiao, C. He, Z. F. Yang, E. Q. Chen, H. J. Lu, X. H. Li and Y. F. Tu, *Chin. J. Polym. Sci.*, 2022, **40**, 584–592.

55 J. Scheirs and T. E. Long, *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*, John Wiley & Sons, 2003.

56 H. Jacobson and W. H. Stockmayer, *J. Chem. Phys.*, 1950, **18**, 1600.