

Synthesis of Cyclic Oligo(ethylene adipate)s and Their Melt Polymerization to Poly(ethylene adipate)*

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Abstract We present here the first synthesis of cyclic oligo(ethylene adipate)s (COEAs) *via* pseudo-high dilution condensation reaction of adipoyl chloride with ethylene glycol, and the synthesis of corresponding poly(ethylene adipate) (PEA) *via* the melt polymerization of COEAs. The structure of COEAs was characterized and proved by ¹H-NMR and MALDI-TOF mass measurements. The effects of organic base, reaction temperature and the ratio of adipoyl chloride to ethylene glycol on the yield of COEAs were studied, and the optimum reaction condition was revealed. PEA, a diacid and diol based semi-crystalline green aliphatic polyester, was synthesized by the melt polymerization of COEAs using Ti(*n*-C₄H₉O)₄ as catalyst and 1,10-decanediol as initiator at 200 °C, which follows the polycondensation-coupling ring-opening polymerization method. Our strategy should be applicable to the synthesis of versatile aliphatic polyesters based on diacid and diol monomers, which have potential applications as biocompatible and biodegradable materials.

Keywords Cyclic oligoesters; Pseudo-high dilution reaction condition; Polycondensation-coupling ring-opening polymerization; Aliphatic polyesters

INTRODUCTION

Biodegradable polymers have attracted great research interests recently due to their green characters by reducing the pollution resulting from plastic wastes, and as renewable resources for polymer manufacturing^[1–3]. Aliphatic polyesters are one class of the most attractive biodegradable polymers used in biomedical applications since they possess a wide range of mechanical properties and bioactivity, depending on their structures and functional groups^[4]. With the chemical and crystal structure similar to polyethylene, polyesters based on aliphatic diacid and diol, such as poly(ethylene adipate) (PEA), poly(butylene adipate) (PBA), poly(ethylene succinate) (PES) and poly(butylene succinate) (PBS), are used in food packaging, agriculture or disposable item, and their properties can be tuned by the copolymerization with other polyesters^[5–10].

Typically, these polyesters are synthesized *via* step-growth condensation polymerization from corresponding dicarboxylic acids (or their diesters) and diols in the melt. However, since the polyesters will degrade significantly at traditional condensation polymerization temperature (~250 °C), they are usually synthesized at relatively low temperature (~200 °C) to avoid decomposition^[11]. At such condition, polyesters with molecular weight of a few thousand Dalton are obtained due to the slow polymerization rate. The chain extension method is thus used to obtain high molecular weight copolyesters by reacting with di- or multi-

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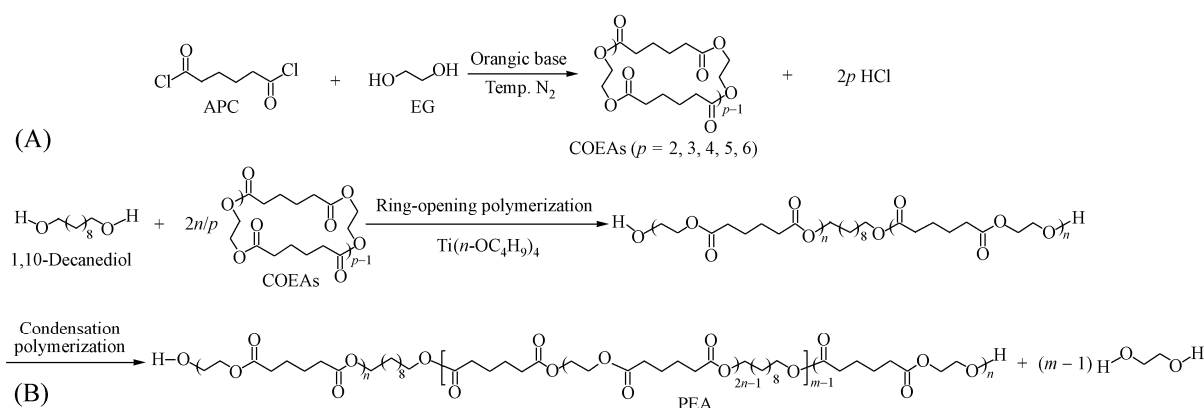
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functional chain extension reagents, affording copolyesters with good mechanical properties to be used as plastics or elastomers^[12–14]. However, this method will introduce other functional groups in the polyesters, which change their properties significantly.

Recently, ring-opening polymerization (ROP) of cyclic oligoesters has been considered to be an efficient approach to synthesize diacid and diol based polyesters^[15]. Compared to condensation polymerization, this process has the merits of fast polymerization rate, high molecular weight of polyesters, no generation of small molecule byproducts, and offers the chance to facilely tune polymer composition and synthesize block copolymers^[16–18]. Recently we found that the polymerization mechanism was not just a ROP process, but an *in situ* cascade polycondensation-coupling ring-opening polymerization (PROP) process when diols were used as initiators^[19–21]. On the other hand, most of the reported works are focused on the synthesis of semi-aromatic polyesters^[16, 22, 23], while few study their application in the synthesis of aliphatic polyesters. The problem lies in the obstacle to obtain corresponding aliphatic cyclic oligoesters^[24, 25].

There are three ways to obtain cyclic oligoesters: (1) extraction from their linear counterparts, which contain a few percent of cyclic oligoesters^[26]; (2) cyclo-depolymerization (ring-chain equilibration reaction) from their linear counterparts, which gives cyclic oligomers with good yield at high temperature in dilute solution^[27, 28]; (3) the pseudo-high dilution condensation reaction developed by Brunelle *et al.* via coupling of diacyl chlorides and diols^[16]. The last method produces cyclic oligoesters with high purity without contamination of linear oligomers. However, to our knowledge, this method has not been applied to the synthesis of aliphatic cyclic oligoesters.

In this work, we would like to explore the approach to synthesize aliphatic cyclic oligoesters *via* pseudo-high dilution condensation reaction method. Since poly(ethylene adipate) (PEA) is a typical aliphatic polyester with good biocompatibility and biodegradable properties, and widely used in polyurethane coatings^[29, 30], its corresponding cyclic oligoesters, cyclic oligo(ethylene adipate)s (COEAs) were chosen as the model compounds for synthesis and polymerization studies. The synthetic route is presented in Scheme 1. The effects of the organic base (amines), reaction temperature, feeding ratio of adipoyl chloride to ethylene glycol on COEAs' yield were systematically investigated. In addition, the obtained COEAs were polymerized to test whether PEA could be synthesized, and the obtained PEA's properties were roughly measured.



Scheme 1 The synthetic route of cyclic oligo(ethylene adipate)s (COEAs) (A) and their polymerization to poly(ethylene adipate) (PEA) *via in situ* cascade polycondensation-coupling ring-opening polymerization process (B)

EXPERIMENTAL

Materials

Adipoyl chloride (APC) (XiaQing Chemical of Changzhou, 99%) was purified by vacuum distillation. Ethylene glycol (EG) (Sinopharm Chemical, 98%) was purified by vacuum distillation after being stirred with calcium hydride overnight. 1,4-Diazabicyclo[2.2.2]octane (DABCO) (Chem Greatwall of Wuhan, 99%) was purified by

sublimation in vacuum. Triethylamine (Et_3N) (Sinopharm Chemical, A.R.), pyridine (Qiangsheng Chemical of Suzhou, A.R.), dichloromethane (CH_2Cl_2) (Qiangsheng Chemical of Suzhou, A.R.), and tetrahydrofuran (THF) (Qiangsheng Chemical of Suzhou, A.R.) were purified by stirring with calcium hydride overnight and then distilled under nitrogen. Ammonium hydroxide (Sinopharm Chemical, 25%–28%), 4-dimethylaminopyridine (DMAP) (Alfa Aesar, 99%), 1,10-decanediol (J&K, 98.5%) and titanium tetrabutoxide ($\text{Ti}(\text{n-C}_4\text{H}_9\text{O})_4$) (Alfa Aesar, 98%) were used as received.

Synthesis of Cyclic Oligo(ethylene adipate)s (COEAs)

The cyclic oligo(ethylene adipate)s (COEAs) were synthesized *via* a pseudo-high dilution reaction as presented in Scheme 1(A). A general experimental procedure is as follows: into a 500 mL three-necked flask with a magnetic stirrer, condenser and nitrogen inlet was charged with a solution of organic base (served as catalyst and neutralizer) in 200 mL of dichloromethane at preset temperature. Cyclization reactions were carried out by the addition of a mixture solution of adipoyl chloride and ethylene glycol in 10 mL of CH_2Cl_2 and 10 mL of THF. After the reaction was quenched with ammonium hydroxide (5 mL), the solution was filtered, and the aqueous layer was extracted with dichloromethane (60 mL for 3 times). The organic layer was washed with dilute HCl and deionized water and then the solvent was removed. Cyclic oligomers were obtained by column chromatography (eluent: 4% acetone in dichloromethane, retention factor (R_f): 0.35). The product was dried under vacuum at 30 °C for 12 h, and obtained as a white solid. Melting point (mp): 46.8–60.5 °C; $^1\text{H-NMR}$ (600 MHz, CDCl_3 , 25 °C, δ) 4.29–4.31 (m, 4H, $\text{OCH}_2\text{CH}_2\text{O}$), 2.34–2.39 (m, 4H, $\text{OOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}$), 1.67–1.69 (m, 4H, $\text{OOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}$).

Synthesis of Poly(ethylene adipate) (PEA)

For a typical polymerization process, cyclic oligo(ethylene adipate)s (monomer) and 1,10-decanediol (initiator) with the ratio of 10/1 (*W/W*) were charged in a three-necked flask with mechanical stirrer and nitrogen inlet. The reactor was immersed in a salt bath controlled at 200 °C for 5 min under nitrogen atmosphere, and then $\text{Ti}(\text{n-C}_4\text{H}_9\text{O})_4$ (0.2 wt%) was introduced to start the polymerization. The mixture was polymerized for 300 min, subsequently quenched to room temperature. The obtained PEA was subjected to gel permeation chromatography (GPC) measurement without further purification.

Instruments

^1H nuclear magnetic resonance (NMR) spectrum was recorded on an Agilent Technologies 600 MHz DD2 spectrometer with PFG $^1\text{H}/^{19}\text{F}/\text{X}$ probe at 25 °C, using deuterated chloroform as the solvent and tetramethylsilane (TMS) as the internal reference. Number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymers were determined by gel permeation chromatography (GPC) using a size exclusion column TOSOH HLC-8320 equipped with refractive index and UV detectors using two TSKgel Super Mutipore HZ-N ($\phi 4.6$ mm $\times$ 150 mm, 3 μm beads size) columns arranged in series, which could separate polymers in the molecular weight range of 500– 1.9×10^5 Da. THF was used as the eluent with a flow rate of 0.35 $\text{mL}\cdot\text{min}^{-1}$ at 40 °C. Data acquisition was performed using EcoSEC software, and molecular weights were calculated relative to polystyrene standards. All samples ($1.0 \text{ mg}\cdot\text{mL}^{-1}$) were passed through 0.45 μm PTFE filter before analysis. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum was acquired on a Bruker Ultraflex-Treme TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd:YAG laser (355 nm). All spectra were recorded in reflective mode. *Trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, Aldrich, > 99%) was used as matrix ($20 \text{ mg}\cdot\text{mL}^{-1}$ in CHCl_3) while sodium trifluoroacetate as the cationization agents ($10 \text{ mg}\cdot\text{mL}^{-1}$ in ethanol). The matrix and cationization agents were mixed in the ratio of 10/1 (*V/V*). The sample preparation involved depositing 0.5 μL of matrix and salt mixture on the wells of a 384-well ground-steel plate, depositing 0.5 μL of the sample ($10 \text{ mg}\cdot\text{mL}^{-1}$ in CHCl_3) on a spot of dry matrix, and adding another 0.5 μL of matrix and salt mixture on top of the dry sample. After evaporation of the solvent, the plate was inserted into the MALDI source. The mass scale was calibrated externally using the peaks obtained from protein standard, and the data were analyzed by Bruker's flexAnalysis and PolyTool software. Thermogravimetric analysis (TGA) was carried out at a heating rate of 10 $\text{K}\cdot\text{min}^{-1}$ from

room temperature to 400 °C under a continuous nitrogen flow of 50 mL·min⁻¹ with a TA Instrument SDT-2960TG/DTA. The temperature of thermal degradation (T_d) was measured at the point of 5% weight loss relative to the weight at room temperature. Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC 2010 within temperature range from -80 °C to 100 °C at a scanning rate of 10 K·min⁻¹ under nitrogen atmosphere with the samples sealed in aluminum pans. Films (~0.5 mm thick) were pressed between two PTFE sheets at 70 °C and 10 MPa for 4 min before immediately quenching in a cold press at room temperature under a pressure of 10 MPa. The obtained sheets were directly used for characterization. Dumbbell-shaped tensile-test specimens (central portion, 2.96 mm × 0.5 mm thick; gauge length 18 mm) were cut from the sheets and conditioned at room temperature for 24 h. Tensile test was carried out on a universal tensile test machine (KJ-1065B, Kejian-tech) with a 50 N load cell at a cross-head speed of the tensile measurement of 10 mm·min⁻¹.

RESULTS AND DISCUSSION

The first report of the synthesis of alkylene phthalate cyclic oligomers *via* pseudo-high dilution reaction condition was as described by Brunelle *et al.* based on the amine-catalyzed reaction of aromatic acyl chlorides with diols^[16]. The yield of the alkylene phthalate cyclic oligomers was strongly affected by the structure of the amine catalyst, and the highest yield was obtained when sterically unhindered amine such as quinuclidine and 1,4-diazabicyclo[2.2.2]octane (DABCO) was used. To reduce the consumption of expensive DABCO, optimization of cyclization condition eventually leads to a process, which uses catalytic amounts of DABCO in conjunction with stoichiometric quantities of triethylamine (serves as the neutralizer), producing up to 60%–80% yield of cyclic oligo(butylene terephthalate)s (COBTs). Following similar synthetic procedure, the attempts to synthesize cyclic oligo(ethylene adipate)s (COEAs) were tried *via* pseudo-high dilution condensation reaction of adipoyl chloride and ethylene glycol as shown in Scheme 1(A), and the effects of different reaction conditions on COEAs' yield are summarized in Table 1.

Table 1 The yields of COEAs under different reaction conditions ^a

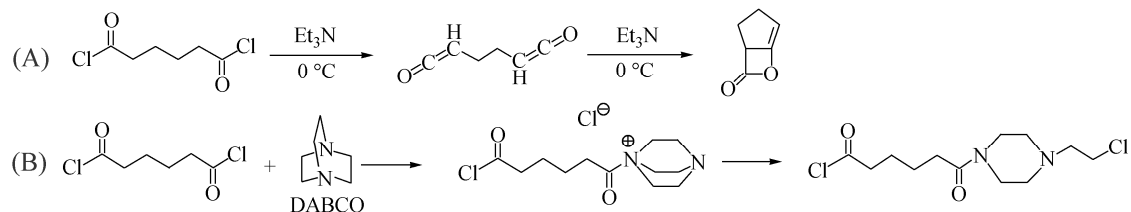
Entry	Organic base ^b	Feeding molar ratio ^c	T (°C)	Yield ^d (%)
1	DABCO + Et ₃ N	1/1/0.1/2	0	Nd ^e
2	DMAP + Et ₃ N	1/1/0.1/2	0	Nd ^e
3	Pyridine	1/1/2.4	0	11
4	Pyridine	1/1/2.4	20	17
5	Pyridine	1/1/2.4	40	23
6	Pyridine	1.1/1/2.4	40	31
7	Pyridine	1.2/1/2.4	40	28

^a All reactions were run on a 0.02 mol scale, addition time of 60 min *via* pseudo-high dilution reaction process; ^b Catalyst and 2 equiv. neutralizer; ^c Feeding molar ratio of APC/EG/organic base; ^d Isolated yield; ^e Not detected

Due to the higher reactivity of adipoyl chloride over that of terephthaloyl chloride (TPC), the reaction of adipoyl chloride with diols such as ethylene glycol is much faster than that of TPC. Thus it was anticipated that cyclic oligo(ethylene adipate)s (COEAs) could be prepared following Brunelle's way using DABCO and triethylamine as organic base. However, no trace of COEAs was detected (entry 1 in Table 1). When DMAP was used as catalyst (entry 2 in Table 1), which is an efficient catalyst for the synthesis of aromatic cyclic oligoesters, the same negative result was observed. These results suggest that significant side reactions coexisted during the reaction when DABCO, triethylamine or DMAP was used as the organic base.

As revealed by Taggi *et al.*^[31], Paul *et al.*^[32] and Hyatt and Raynolds^[33], lactone is a side product when aliphatic acyl chloride is mixed together with Et₃N, as illustrated in Scheme 2(A), by the dehydrohalogenation reactions of α -protons with chlorides. The yield of lactone increases with the strength of base. For aromatic acyl chlorides like terephthaloyl chlorides, there is no such side reaction since no α -proton exists. This is why Brunelle's method works for the synthesis of aromatic cyclic oligoesters. On the other hand, when unhindered amine (DABCO) is used as organic base, it can react with APC to form an acylammonium salt, which

subsequently decomposes to an amide as the subordinate side reaction, as illustrated in Scheme 2(B)^[16]. These side reactions are significant at about 0 °C due to the high reactivity of aliphatic acyl chlorides, and strongly change the ratio of diacyl chlorides to diols, resulting in low or no yield of cyclic oligomers.



Scheme 2 Plausible side reactions during the synthesis of COEAs with organic base

It is speculated that the synthesis of aliphatic cyclic oligoesters can proceed as in Scheme 1(A) if the above two side reactions can be suppressed. Following this, a much weaker organic base, pyridine (pK_b : 8.79 versus 3.25 for Et₃N) was chosen as organic base during the reaction. In this case, the side reaction as shown in Scheme 2(B) can be ignored while that in Scheme 2(A) should be significantly retarded. As predicted, COEAs were detected with an isolated yield of 11% at reaction temperature of 0 °C in the presence of 240 mol% pyridine (entry 3 in Table 1). Here pyridine serves with two effects: to neutralize the HCl liberated in the reaction and also as a nucleophilic catalyst.

The yields of COEAs under different reaction conditions using pyridine as organic base were investigated to find the optimum reaction conditions for the synthesis of COEAs. The yields of COEAs under reaction temperature ranging from 0 °C to 40 °C were separately examined, and the results are listed in Table 1 (entries 3–5). The results indicate that the highest yield was achieved at 40 °C, unlike that in Brunelle's reported work where 0 °C led to the best yield^[16]. As high efficient catalyst DABCO was used in their cases, side reactions with terephthaloyl chloride went up with elevated temperature. However, in our case, since such side reaction can be ignored and pyridine is a much weaker catalyst than DABCO, a relative higher temperature is necessary to enhance the reaction rate for a higher yield of COEAs, as the faster the reaction rate of acyl chlorides with diols is, the higher the yield of cyclic oligoesters should be obtained at pseudo-high dilution reaction conditions.

Due to the contamination of moisture in solvents and reagents, which may react with the acyl chloride, usually a slightly higher molar ratio than 1:1 for acyl chloride to diol is applied. The yields under different molar ratios of adipoyl chloride (APC) to ethylene glycol (EG) (ranging from 1.0 to 1.2) were investigated (entries 5–7 in Table 1). The results indicate that at APC/EG molar ratio of 1.1, the highest yield of 31% was achieved, while at 1.0 or 1.2, 25% or 28% isolated yields was achieved, respectively. Further increment in APC/EG ratio would lead to poor yields, since the stoichiometry balance is destroyed. After extensive studies of the effects of reaction parameters on COEAs' yields, the optimized reaction condition was obtained as following: a 1.1/1 ratio of APC/EG in CH₂Cl₂ under reflux condition with 60 min reaction time using pyridine as organic base (240 mol%). At this condition, cyclic oligo(ethylene adipate)s (COEAs) were prepared in a relative high yield *via* pseudo-high dilution condensation reaction.

The structure of the above cyclic oligoesters was confirmed by ¹H-NMR. Figure 1 shows the typical ¹H-NMR spectrum of COEAs. Since the COEAs are a mixture of cyclic oligoesters with different ring sizes, the protons from similar chemical position but different ring sizes may show slightly different chemical shifts, as we previously reported in the observation of pure cyclic oligo(trimethylene terephthalate)s with different ring sizes^[34]. The peaks at chemical shift around $\delta = 4.29$ (peak a, $\text{OCH}_2\text{CH}_2\text{O}$) are assigned to the protons from EG segments, while the peaks at $\delta = 2.36$ (peak b, $\text{OOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}$) and peaks at $\delta = 1.69$ (peak c, $\text{OOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}$) are assigned to the protons from APC segments. The ratio of the integration value of corresponding peak areas (1:1:1) fits well with the theoretical value within the margin of error of the NMR technique, indicating the high purity of the cyclic oligoesters.

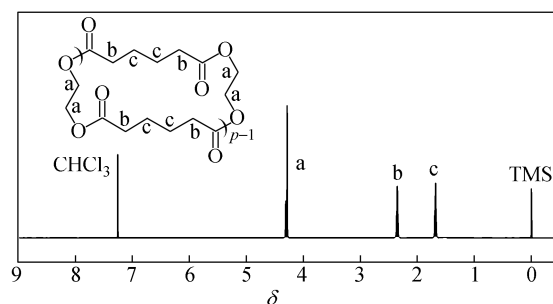


Fig. 1 ^1H -NMR spectrum of COEAs (solvent: CDCl_3)

Figure 2 is the MALDI-TOF mass spectrum of the COEAs, which further proves that the obtained product is a mixture of cyclic oligoesters with different ring sizes. The observed main peaks can be assigned to sodium cationized COEAs with different ring sizes, while the small peaks below 800 (m/z) are from the matrix. For example, the peak at 367.18 (m/z) is assigned to $[\text{dimer}+\text{Na}]^+$ ($\text{C}_{16}\text{H}_{24}\text{O}_8\text{Na}$, theoretical value 367.35), as shown in the enlarged figure for the peak. Cyclic oligoesters with degree of oligomerization up to 6 are observed, among which the trimer content is the highest.

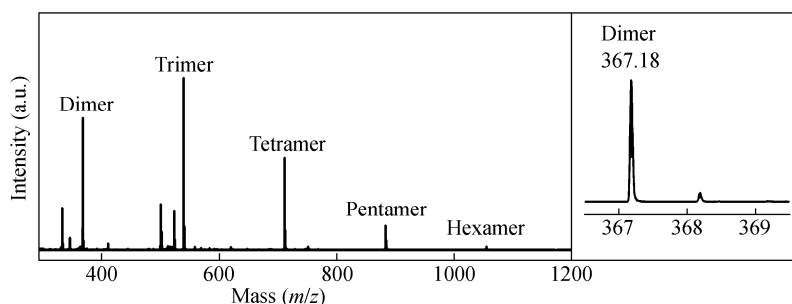


Fig. 2 MALDI-TOF mass spectrum of COEAs (matrix: DCTB)

Using 1,10-decanediol as initiator and COEAs as monomer (weight ratio 1:10), melt polymerization was carried out to examine whether these COEAs could be used as monomers for the synthesis of PEA. The GPC curves of resultant PEA and corresponding monomer COEAs as reference are presented in Fig. 3, using THF as eluent. After melt polymerization, a single peak at a much lower retention volume is observed, indicating the successful synthesis of PEA. The estimated number-average molecular weight and polydispersity index of resultant PEA are 18.9 kDa and 1.60, respectively.

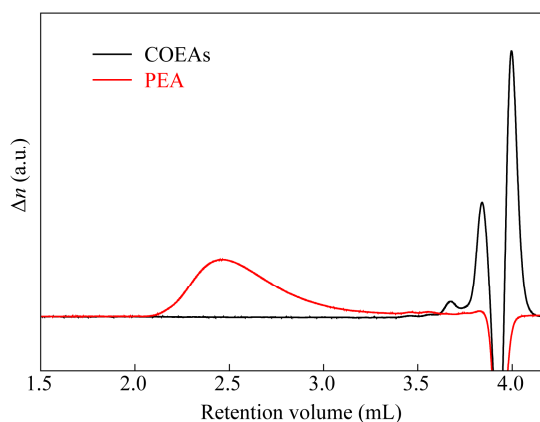


Fig. 3 GPC curves of synthesized COEAs and PEA (eluent: THF)

The theoretical molecular weight of PEA obtained by ROP can be calculated by the monomer to initiator ratio with the conversion of monomer. The molecular weight of PEA revealed from GPC was much higher than theoretical value (1.9 kDa at full conversion), indicating that after ring-opening polymerization, which afforded the di-hydroxyl end-functionalized PEAs, polycondensation between these polyesters proceeded by losing diols, which significantly increased the molecular weight of polyesters, as illustrated in Scheme 1(B). This *in situ* cascade polycondensation-coupling ring-opening polymerization (PROP) process was also observed in the synthesis of polyesters or poly(ether ester) multiblock copolymers when using dihydroxyl end-functionalized initiators and cyclic oligoesters as monomers^[19–21].

Since molecular weight obtained from GPC measurement is the apparent value, which is related to polystyrene standards, PEA sample with relative number-average molecular weight of 18.9 kDa was subjected for an improved quantitative ¹H-NMR analysis using end-group estimation method and the optimum parameters we recently established^[35]. Figure 4 is the quantitative ¹H-NMR spectrum of PEA sample. The corresponding assignment of peaks to the chemical structure is shown at the top of figure. Two peaks (peaks g and h) from different end groups (OCH₂CH₂(g)OH and CH₂CH₂CH₂(h)OH) appeared, indicating that transesterification occurred in the polymerization process. The peak at chemical shift of $\delta = 3.83$ (peak g) corresponds to the end group (CH₂OH) of EG, while peak h ($\delta = 3.68$) belongs to the terminal group (CH₂CH₂CH₂OH) of 1,10-decanediol. The total repeating units of ethylene adipate (EA) (N_{EA}) and decamethylene adipate (DA) (N_{DA}) in polymer can be calculated by integration ratio of chain end groups to corresponding groups of repeating units by ¹H-NMR spectrum. Here we choose the chain end groups of g and h, peak a of EG segment at $\delta = 4.27$, and peak d of 1,10-decanediol segment at $\delta = 4.05$ for calculation using the following equations:

$$\frac{I_g + I_h}{I_a} = \frac{4}{4N_{EA}} \quad (1)$$

$$\frac{I_g + I_h}{I_d} = \frac{4}{4N_{DA}} \quad (2)$$

where I_a , I_d , I_g and I_h are the integration values for the corresponding peak at a, d, g, and h, respectively. The total number-average molecular weight for the whole polymer (M_n) is 14.8 kDa calculated by $M_n/Da = 172 \times N_{EA} + 284 \times N_{DA}$, which is slightly lower than GPC result (18.9 kDa).

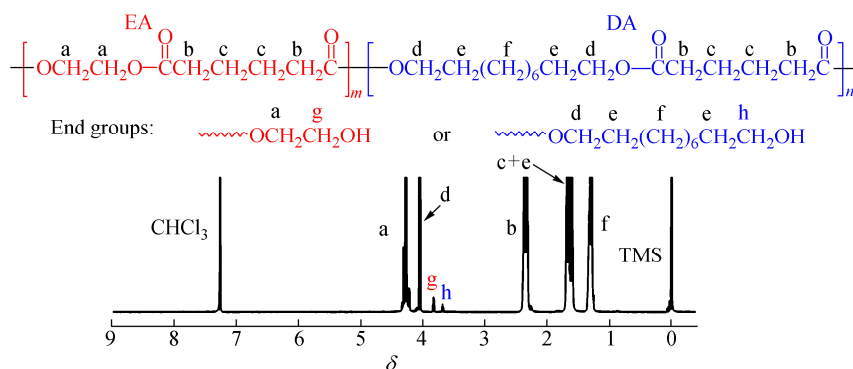


Fig. 4 ¹H-NMR spectrum of synthesized PEA (solvent: CDCl₃)

The thermal properties of COEAs and PEA were studied by TGA and DSC, with the results listed in Table 2. Figure 5 shows the TGA curves of COEAs and PEA under nitrogen, in which they show moderate thermal stability. A single weight loss stage is observed for both the samples. The degradation temperature (T_d at 5% weight loss) under nitrogen is 204 and 313 °C for COEAs and PEA, respectively. Compared to their aromatic counterparts, the degradation temperatures of COEAs and PEA are much lower (~100 °C lower) due to the absence of aromatic ring, which significantly increases the thermal stability of cyclic oligoesters and polyesters by the conjunction of benzene ring with ester bonds.

Table 2 Thermal and mechanical properties of COEAs and PEA

Sample	T_d (°C)	T_g (°C)	T_c (°C)	T_m (°C)	Young's modulus (MPa)	Elongation at break (%)	Tensile strength (MPa)
COEAs	204	—	30	56	—	—	—
PEA	313	−44	−3	39	66.9 ± 2.7	16.3 ± 1.5	9.2 ± 1.1

T_d : 5% weight loss temperature with a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$ under nitrogen; T_g , T_c , and T_m were determined by DSC measurement (scanning rate $10 \text{ K} \cdot \text{min}^{-1}$).

Figure 6 presents the DSC curves of COEAs and PEA. The melting transition peak temperature (T_m) of COEAs determined from the second heating process is 56°C , while the crystallization temperature (T_c) determined is around 30°C , at a scanning rate of $10 \text{ K} \cdot \text{min}^{-1}$. No glass transition temperature is detected for these cyclic oligomers. For PEA, the glass transition temperature (T_g) determined during the second heating is -44°C , slightly lower than that reported (about -43°C)^[36]. The broad peak at around -3°C in cooling curve is the exothermic crystallization peak. The melting temperature for PEA determined is around 39°C , comparable to those reported by others^[37–39]. The enthalpy obtained is $11 \text{ J} \cdot \text{g}^{-1}$, from which the crystallinity of PEA determined is 9% ($\Delta H_{m,100\%} = 118 \text{ J} \cdot \text{g}^{-1}$)^[38]. The low crystallinity of PEA further proves that the inclusion of 1,10-decanediol segments in PEA main chain reduces the crystallization rate of PEA.

The typical stress-strain curves of PEA are presented in Fig. 7, and the mechanical properties are listed in Table 2. No characteristic yield point is observed for PEA samples while only a brittle failure at strain of $\sim 16\%$ is observed. The average Young's modulus determined is 66.9 MPa for PEA.

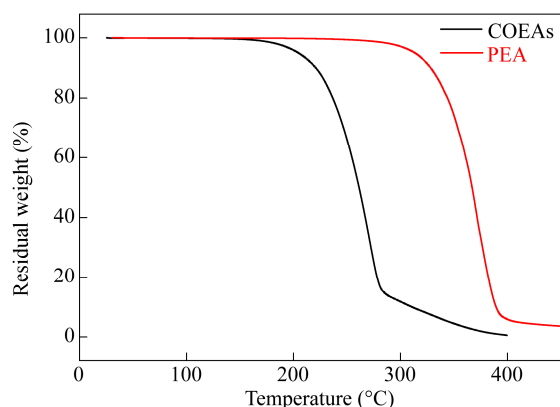


Fig. 5 TGA curves of COEAs and PEA with a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$ under nitrogen

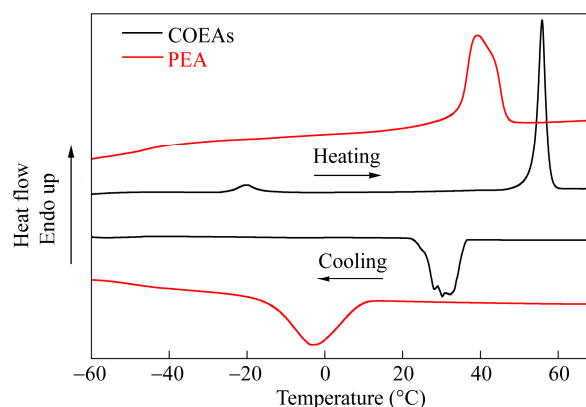


Fig. 6 DSC 2nd heating curves and 1st cooling curves of COEAs and PEA with a scanning rate of $10 \text{ K} \cdot \text{min}^{-1}$ under nitrogen

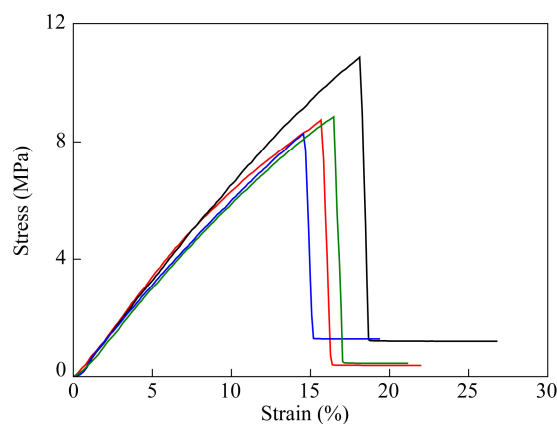


Fig. 7 Stress-strain curves of PEA samples

CONCLUSIONS

In summary, we demonstrate that cyclic oligo(ethylene adipate)s (COEAs) can be synthesized *via* pseudo-high dilution condensation reaction of adipoyl chloride with ethylene glycol using pyridine as organic base. The optimum reaction condition was revealed to be at the molar ratio of 1.1:1:2.4 for adipoyl chloride to ethylene glycol to pyridine at 40 °C. The obtained cyclic oligo(ethylene adipate)s (COEAs) are a mixture of cyclic oligomers with different ring sizes, which can undergo PROP to afford PEA when using 1,10-decanediol as an initiator. The thermal properties of COEAs and PEA were roughly studied, and the results indicate that the inclusion of 1,10-decanediol segments reduces the crystallization rate and crystallinity of PEA. Our approach affords a facile synthetic method to obtain biodegradable polyesters.

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