A Potential Alternative to Polystyrene: Ring-opening Terpolymerization of Different Epoxides with Phthalic Anhydride Using Metal-free Dual Catalysts

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Abstract
A series of semi-aromatic polyesters named as Poly(PO-CHO-PA) were facilely synthesized via ring-opening terpolymerization of bio-based cyclohexane oxide (CHO)/propylene oxide (PO)/phthalic anhydride (PA) using economical U1/PPNCl as dual catalyst. The proportion of CHO-PA and PO-PA segments in polymer can be readily altered by changing the feed ratio of CHO/PO because the reactivity ratios of CHO and PO with PA calculated by Fineman-Ross method are comparable. All synthesized amorphous polyesters with various compositions show one Tg ranging from 62 °C to 133 °C. Significantly, the mechanical, thermal and barrier properties of these amorphous semi-aromatic polyesters are also adjustable and investigated for the first time. The results indicate the semi-polyesters exhibit superior thermostability (T65g ranging from 306 °C to 323 °C) and high tensile strength (40.21−55.7 MPa) that is comparable with polystyrene (PS). Furthermore, Poly(PO-CHO-PA) films possess a promising prospect as packaging materials because of its colorless and highly transparent nature, along with low oxygen and water vapor transmission rate. All above performances may guarantee its potential alternative to commercial PS.

Keywords Aromatic polyester; Ring-opening polymerization; Metal-free catalyst; Polystyrene; Barrier properties

Citation: Lin, L. M.; Xu, Y. H.; Shen, M.; Liang, J. X.; Wang, S. J.; Xiao, M.; Meng, Y. Z. A potential alternative to polystyrene: ring-opening terpolymerization of different epoxides with phthalic anhydride using metal-free dual catalysts. Chinese J. Polym. Sci. 2021, 39, 337–343.

INTRODUCTION
Polyesters are a class of attractive polymers, especially the aromatic polyesters constituted by benzoic ester type repeat units, which are widely used as films, fibers, resins, due to their excellent thermal stability and mechanical properties as well as inexpensiveness. However, the aromatic polyesters are typically synthesized by step-growth polymerization of diols and aromatic dicarboxylic acids or diesters, requiring rigorous conditions of high temperature and high vacuum. On the other hand, the minimal available cyclic aromatic monomers and complicated steps to obtain functionalized polyesters limit the synthesis method of ring-opening polymerization (ROP) of cyclic aromatic esters. Nevertheless, ring-opening alternating copolymerization (ROAC) of epoxides and anhydrides can easily adjust the species and get miscellaneous polyesters with functional modifications. So ROAC of different epoxides and anhydrides is more atom-economical, energy-saving and controllable. What is more, most of the epoxides and anhydrides are commercially available, but also can be derived from renewable sources, including cyclohexane oxide (CHO), propylene oxide (PO) and phthalic anhydride (PA).

Since the middle of the last century, a variety of metal complexes have been developed for ROAC of epoxides and anhydrides. Therein, the cobalt and chromium salen complexes exhibited outstanding catalytic efficiency and selectivity. Most of the polyesters are used as food packaging or sensitive devices, which demand colorless and minimal content of metal element. Therefore, there has been a rapidly increasing attention in employing green metal-free catalysts with high activity and selectivity for ROAC of epoxides and anhydrides. Firstly, organic bases, like quaternary onium salts, tertiary amines, and phosphazene were successively employed as a single catalyst for ROAC, but they did not display satisfactory catalytic efficiency. Later, Zhang and Li’s group consecutively reported the usage of organoboron compounds/quaternary onium salts in this ROAC process with marvelous activity and stereoselectivity. Recently, our group has developed an economical and effective dual organocatalyst, composed of (thio)ureas and organic bases, toward the ROAC of the most commonly used epoxides and anhydrides. A series of polyesters with diverse sequence structures and high ester linkages...
(99%) were synthesized, and the reaction TOF and glass transition temperature of the polymers can reach up to 456 h⁻¹ and 133 °C, respectively. To meet the product property requirement and cost competition to bring aromatic polyesters to market, further improvement in structures and properties design is still needed. The ROAC of different epoxides with anhydrides using salph-Al complex or phosphazene catalysis had been preliminarily researched, but the properties of resultant polyesters had not been explored. In this work, the ring-opening terpolymerization of CHO, PO and PA was designed and carried out using more economical metal-free dual catalyst. Particularly, the performances such as mechanical strength, thermostability, transparency, as well as gas-barrier properties are investigated in detail. From the view point of aforementioned concerns, the synthesized new polyester could be a potential alternative to commercial PS.

EXPERIMENTAL

General Considerations

All chemicals were used as received unless otherwise stated. Cyclohexane oxide (CHO) and propene oxide (PO) were refluxed over CaH₂ for 24 h and vacuum-distilled prior to use. Phthalic anhydride (J&K, 98%) was purified by sublimation. N,N′-dicyclohexylurea (TCI, 98%) and bis(triphenylphosphine)iminium chloride ([PPN]Cl) (Alfa, 97%) were used as received. ¹H-NMR spectra were obtained on a Bruker DRX-500 MHz NMR spectrometer using CDCl₃ as the reference. Molecular weight determinations were carried out using a Waters gel permeation chromatography (GPC) system with chloroform as eluent. The GPC system was calibrated by a series of polystyrene standards with polydispersity of 1.02. The glass-transition temperatures (Tg) were measured by a differential scanning calorimeter (DSC, Netzsch Model 204). The samples were firstly heated at a heating rate of 10 °C/min and then cooled at a cooling rate of 10 °C/min by liquid nitrogen, followed by the second heating. Melt index was tested by a melt flow index meter, according to ASTM D1238-82 standard. The instrument die parameters were diameter of 2.0955±0.0051 mm and length of 8.000±0.025 mm. The test load was 2.16 kg and the temperature was 170 °C. Static tensile performance was tested with a SANS universal testing machine (cmt-4104), according to ASTM D638 standard. The conditions were at 25 °C, 50% of the relative humidity environment and the tensile speed was 50 mm/min. The size of polymer samples was 25 mm × 4.3 mm × 1.0 mm. All samples were allowed to store for 24 h at 25 °C, 50% relative humidity to eliminate the influence of environmental factors. Five samples of each group were tested in parallel and the results were averaged. Oxygen transmittance test (OTR) was carried out with a Y202D oxygen transmittance tester (Guangzhou standard international packaging equipment Co., Ltd.), using Coulomb method (isobaric method) to test oxygen transmittance. According to the ASTM d3985-05 standard, the samples were made into a circle with an area of 50 cm² and tested at 23 °C, 0% of the relative humidity. The average value of each sample was obtained after two parallel measurements. Water vapor transmittance test (WVTR) was performed at PERMATEX Model 3/61 (MOKANG Co., Ltd., USA), using infrared sensor method to test water vapor transmittance. According to the ISO 15106-2 standard, test sample was measured three times in parallel at 23 °C and 85% relative humidity.

General Procedure of Polymerization

Polymerizations were performed in vial using an external heating bath. The vial was charged with a predetermined amount of N,N′-dicyclohexylurea (0.05 mmol, 1 equiv.), bis(triphenylphosphine)iminium chloride (0.05 mmol, 1 equiv.), epoxide (CHO and PO) (10 mmol, 200 equiv.) and phthalic anhydride (5 mmol, 100 equiv.), which were kept stirring for 5 min at room temperature in an N₂-filled glovebox. The vial was sealed, taken out of glovebox, and then immersed in the heating bath under the predetermined temperature. After equilibration at the desired polymerization temperature, the polymerization started. After a desired period of time, the vial was removed from heat block and a 0.2 mL of aliquot was taken from the reaction mixture and prepared for ¹H-NMR analysis. Then the mixture was dissolved in CHCl₃ and precipitated into 10-fold excess of methanol or hexane, filtered, washed with methanol or hexane to remove unreacted monomer, and dried in a vacuum oven at room temperature to a constant weight.

RESULTS AND DISCUSSION

The most active dual catalyst U1/PPNCl as shown in Scheme 1, was selected for the ring-opening terpolymerization of CHO/PO/PA. The reaction performed at U1/PPNCl/CHO/PO/PA = 1/1/100/100/100 was monitored by ¹H-NMR to calculate the conversion of PA and the formed segment ratio of CHO/PA/PO/PA over time. Fig. 1 indicates the successive enchainment of PO-PA and CHO-PA pairs. The CHO-PA/PO-PA ratio in the terpolymer (Poly(PO-CHO-PA)) increases slightly from 1/1.4 to 1/1.2, indicating that CHO and PO copolymerize competitively with anhydride to some content.

In order to quantitatively compare the reactivity of CHO and PO, Fineman-Ross method was employed to calculate the reactivity ratio of CHO and PO. A series of reactions with different CHO/PO monomer feed ratios were performed, and the monomer conversion was kept low to ensure the accuracy of calculation. As shown in Table 1, F is the monomer feed

![Scheme 1](https://doi.org/10.1007/s10118-020-2495-6)
ratio of CHO/PO and \( f \) is the ratio of CHO-PA/PO-PA in the product. The rate constant \( k_{\text{CHOCHO}} \) or \( k_{\text{POPO}} \) is defined as the insertion rate of CHO or PO into the CHO-PA chain end, while \( k_{\text{POPO}} \) or \( k_{\text{CHOCHO}} \) is the rate of PO or CHO insertion into PO-PA chain end, respectively. The monomer reactivity ratio of CHO is \( r_1 = k_{\text{CHOCHO}}/k_{\text{POPO}} \) and the counterpart of PO is \( r_2 = k_{\text{POPO}}/k_{\text{CHOCHO}} \). The above physical quantities can well satisfy the Fineman-Ross formula (Eq. 1) as shown in Fig. 2; the plot of \( (f - 1)/F \) to \( f/F^2 \) exhibits a good linear fitting. From the curve intercept and slope, we can get \( r_1 = 0.30 \), \( r_2 = 0.88 \), which indicate that the competitive rate of PO is slightly greater than that of CHO, but both are less than 1. Therefore, it implies a random structure of resultant polymer, and the proportion of PO-PA sequence in the polyester is slightly greater than that of CHO-PA sequence.

\[
\frac{(f - 1)}{F} = -\frac{r_2}{r_1^2} f + r_1
\]  

(1)

### Table 1

| Entry | U1/PPNCl/CHO/PO/PA | PA (1 min) conv. (%) | \( f \) | \( f^2 \) |
|-------|---------------------|----------------------|------|--------|
| 1     | 1/1/150/50/100     | 6                    | 3.00 | 1.50   |
| 2     | 1/1/133/67/100     | 5                    | 1.98 | 1.20   |
| 3     | 1/1/100/100/100   | 6                    | 1.00 | 0.67   |
| 4     | 1/1/67/133/100    | 6                    | 0.50 | 0.38   |
| 5     | 1/1/50/150/100    | 7                    | 0.33 | 0.31   |

* Copolymerizations were carried out at 110 °C in bulk in vial; PA was sublimated as with otherwise mentioned. \(^{a}\) Molar ratio of CHO and PO in feed. \(^{b}\) CHO-PA/PO-PA content in resultant polymer was determined by \(^{1}H\)-NMR.

When the ratios of CHO/PO and (CHO+PO)/PA were fixed at 1/1, PA cannot be completely converted into polymer due to the high viscosity of the reaction mixture without excess epoxide as solvent in later period (Table 2, entries 1 and 2). Under the same reaction conditions except for excess epoxide (Table 2, entries 3 and 4), the 100% conversion of PA can be afforded. It has been reported that trace of phthalic acid in crude PA can also act as the initiator for the reaction, so the molecular weight of resulting polyester increases significantly in case carefully sublimed PA was used when comparing Table 2 entry 3 with entry 5. When further increasing the monomer/catalyst ratio from 100 to 800 (Table 2, entries 5–7), the molecular weight obviously increases from 17.8 kDa to 45.8 kDa. However, the increasing trend levels off almost when monomer/catalyst ratio further increases to a value higher than 1200 (Table 2, entries 8 and 9). Presumably, this is because it is difficult to completely remove the diacid impurity in PA and the actual initiator ratio in the reaction cannot be decreased anymore. When the ratio of U1/PPNCl/CHO/PO/PA is 1/1/1600/1600/1600, the highest molecular weight reaches 52.2 kDa. In addition, it was found that the ratio of CHO-PA/PO-PA in the resultant terpolymers was always 1/1.2–1.3 when the ratio of CHO/PO/PA was 1/1. Based on these results, the proportion of CHO-PA and PO-PA in terpolymer can be readily tailored by changing the feed ratios of monomers. Hence, fixing the ratio of [CHO+PO]/[PA] at 3200/1600 while varying the monomer ratio of CHO/PO, a series of polyesters with similar molecular weight about 40.1–53.5 kDa were obtained as listed in Table 3.

The DSC curves (Fig. 3) show the obtained Poly(PO-CHO-PA) with only one \( T_g \), demonstrating the amorphous structure of the terpolymers. CHO has a rigid cyclohexyl group, so the Poly(CHO-alt-PA) only containing CHO-PA segment has

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**Fig. 1** In situ \(^{1}H\)-NMR spectra of reaction performed at U1/PPNCl/CHO/PO/PA = 1/1/100/100/100 in bulk at 110 °C with different reaction time.

**Fig. 2** Fineman-Ross plot for monomer reactivity evaluation of CHO/PO/PA terpolymerization.

**Table 2** Copolymerization of CHO/PO/PA catalyzed by U1/PPNCl with different monomer ratios of CHO/PO/PA.

| Entry | U1/PPNCl/CHO/PO/PA | t (h) | PA conv. (%) | \( r_1 \) | \( M_n \) (kDa) | PDI |
|-------|---------------------|------|-------------|------|--------------|-----|
| 1     | 1/1/50/50/100     | 1    | 75          | 1/1.2| 6.80         | 1.36|
| 2     | 1/1/100/100/200  | 2    | 86          | 1/1.3| 11.3         | 1.28|
| 3     | 1/1/100/100/100  | 1    | 100         | 1/1.2| 11.7         | 1.64|
| 4     | 1/1/200/200/200  | 2    | 100         | 1/1.3| 14.7         | 1.64|
| 5     | 1/1/100/100/100  | 1    | 100         | 1/1.3| 17.8         | 1.54|
| 6     | 1/1/500/500/500  | 8    | 100         | 1/1.3| 32.3         | 1.56|
| 7     | 1/1/800/800/800  | 15   | 98          | 1/1.3| 45.8         | 1.66|
| 8     | 1/1/1200/1200/1200| 24   | 100         | 1/1.3| 48.8         | 1.58|
| 9     | 1/1/1600/1600/1600| 30   | 100         | 1/1.3| 52.2         | 1.49|

* Copolymerizations were carried out at 110 °C in bulk in a vial; PA was without sublimation unless otherwise mentioned. \(^{b}\) PA conversion and CHO/PO content in resultant polymer were determined by \(^{1}H\)-NMR. \(^{c}\) \( M_n \) and PDI were determined by GPC. \(^{d}\) PA was with sublimation.
Table 3  Copolymerization of CHO/PO/PA catalyzed by U1/PPNCl using different monomer ratios of CHO/PO.a

| Entry | CHO/PO | CHO-PA/PO-PA ratio b | M_n (kDa)/PDI c | T_g °C | T_{5%}/T_{max} °C | Tensile strength (MPa) | Tensile strain (%) |
|-------|--------|----------------------|-----------------|--------|------------------|------------------------|-------------------|
| 1     | 1/0    | 1/0                  | 42.3/1.47       | 133    | 306/350          | 55.2±1.3               | 5.5±0.1           |
| 2     | 3/1    | 2.5/1                | 40.1/1.59       | 108    | 309/353          | 50.9±1.5               | 6.2±0.1           |
| 3     | 2/1    | 1.8/1                | 44.4/1.59       | 98     | 310/354          | 47.1±1.1               | 7.3±0.2           |
| 4     | 1/1    | 1/1.2                | 50.4/1.58       | 88     | 313/357          | 43.2±1.4               | 8.1±0.1           |
| 5     | 1/2    | 1/2.1                | 40.7/1.57       | 74     | 319/360          | 41.1±0.9               | 8.7±0.3           |
| 6     | 1/3    | 1/3.3                | 53.5/1.58       | 62     | 320/363          | 40.2±0.7               | 8.8±0.1           |
| 7     | 0/1    | 0/1                  | 44.2/1.61       | 55     | 323/370          | 38.2±1.0               | 10.0±0.2          |

a The copolymerizations were carried out at [U1]/[PPNCl]/[CHO+PO]/[PA] = 2/1/3200/1600 at 110 °C in bulk in a vial. PA was sublimated unless otherwise mentioned. The reactions were performed at enough reaction time to ensure conversion of PA>99%. b CHO-PA and PO-PA contents in resultant polymer were determined by 1H-NMR. c M_n and PDI were determined by GPC. d T_g was detected by DSC measurement from the second heating scan at the heating rate of 10 °C/min. e T_{5%}/T_{max} were determined via TGA.

Fig. 3  (a) DSC curves of resultant polymers with different CHO-PA/PO-PA ratios; (b) Plot of the dependence of T_g of copolymers on the ratio of PO-PA segment in copolymers.

The highest T_g of 133 °C, while Poly(PO-alt-PA) only with PO-PA segment shows the lowest T_g of 62 °C. The Poly(PO-CHO-PA) with the higher content of CHO-PA segments possesses higher T_g varying from 62 °C to 133 °C, and there is a good linear relationship between T_g and CHO-PA ratio (Fig. 3). It should be noted that when the ratio of CHO-PA/PO-PA is 1.8/1, the polyester owns a similar T_g to polystyrene about 98 °C.

The thermal degradation performance of Poly(PO-CHO-PA) was investigated by TGA tests. The results in Fig. 4 (Table 3) reveal that all Poly(PO-CHO-PA) samples have only one thermal decomposition peak. The T_{5%}/T_{max} values of Poly(CHO-alt-PA) and Poly(PO-alt-PA) polyesters are 306/350 °C and 333/370 °C, respectively. It can be seen that the thermal degradation temperature of Poly(PO-CHO-PA) gradually increases with increasing the content of PO-PA segment. In general, the thermal degradability of Poly(PO-CHO-PA) is similar to general plastics such as PS (T_{5%} about 300 °C) and polyethylene terephthalate (PET) (T_{5%} about 350 °C). Meanwhile, the melt index of Poly(PO-CHO-PA) (M_n = 44.7 kDa) was tested to be 7.5 g/10min at 170 °C with a load of 2.16 kg, which is higher than that of PS (M_n=12.8 kDa, 5.5 g/10min at 230 °C and 2.16 kg). The above measurements elucidate that Poly(PO-CHO-PA) has splendid thermal stability and melt fluidity and thus is suitable for thermal pro-

https://doi.org/10.1007/s10118-020-2495-6
cessing like PS and PET.

As well known, polystyrene is a rigid and brittle material (tensile strength around 46–60 MPa and elongation at break about 3%–4%).

Coincidentally, Poly(PO-CHO-PA) also exhibits high tensile strength and low elongation at break in static tensile test as shown in Fig. 5 and Table 3. Poly(CHO-alt-PA) with both rigid cyclohexyl and aromatic groups has the highest tensile strength and the lowest elongation at break (55.7 MPa and 5.5%), while Poly(PO-alt-PA) has the lowest tensile strength and the highest elongation at break (40.2 MPa and 8.9%). With increasing the ratio of soft PO-PA segments in polymer, the tensile strength of Poly(PO-CHO-PA) decreases gradually, but the elongation at break increases. In this sense, the mechanical performance of Poly(PO-CHO-PA) can be readily tailored to meet varying applications. Poly(PO-CHO-PA) is colorless and very transparent due to the amorphous structure and usage of metal-free catalyst. It has high light transmittance about 90% detected by UV-Vis-spectrometry (Fig. 6), which is similar to either PS or PMMA (around 90%–93%).

Therefore, this new polyester can be used in packaging materials, foaming materials and illumination equipments. The barrier property is crucial for packaging materials, so the oxygen (OTR) and water vapor permeability (WVTR) were respectively evaluated. The results in Table 4 indicate that the barrier property of Poly(CHO-alt-PA) is slightly better than that of Poly(PO-alt-PA), and the oxygen permeability coefficient (OP) and water vapor permeability coefficient (WVP) of Poly(CHO-PA) with CHO-PA/PO-PA ratio of 1/1.2 is ca. 11.13 cm³/m²/(m²·24h) and 3.55 g·mm/(m²·24h), respectively. Obviously, the barrier properties of Poly(CHO-PA) are comparable to that of PET, and much better than those of other polyesters like poly(lactic acid).

Presumably, this is attributed to the completely amorphous structure and strong secondary interaction strengthened in the presence of aromatic benzene.

Thus, these new semi-aromatic polysters promise great potential application in packaging materials.

**Table 4** OTR, OP, WTR and WVP of the Poly(CHO-alt-PA), Poly(PO-alt-PA) and Poly(PO-CHO-PA).

| Sample           | Thickness (μm) | OTR (cm³/m²/24h) | OP (cm³/m²/(m²·24h)) | WVTR (g·mm/m²·24h) | WVP (g·mm/m²·24h) |
|-------------------|----------------|------------------|-----------------------|---------------------|-------------------|
| Poly(CHO-alt-PA)  | 51±2.5         | 20.75±0.01       | 10.63±0.06            | 5.86±0.05           | 3.00±0.03         |
| Poly(PO-alt-PA)   | 55±3.2         | 20.12±0.01       | 11.33±0.08            | 6.42±0.05           | 3.55±0.05         |
| Poly(PO-CHO-PA)   | 51±4.5         | 22.10±0.01       | 11.35±0.08            | 6.95±0.05           | 3.57±0.05         |

*Oxygen transmission rate (OTR) measurements were performed at a constant temperature of 23 °C under dry conditions according to ASTM D3985-05. The water vapor transmission rate (WVTR) measurements were performed at a constant temperature of 23 °C under 85% RH conditions.

**CONCLUSIONS**

In conclusion, a series of semi-aromatic polyesters Poly(PO-CHO-PA) is proved to be readily synthesized via ring-opening ter-polymerization of CHO/PO/PA using dual catalyst of U1/PPNCl. The reactivity ratios of both PO and CHO are less than 1 as calculated by Fineman-Ross method, leading to a random insertion of PO-PA and CHO-PA segments. The proportions of both CHO-PA and PO-PA in polymer chain are almost same with the feed ratio of monomers; in this sense, the molecular structure of the semi-aromatic polyesters can be designed and adjusted. All synthesized polyesters are amorphous with only one Tg varying from 62 °C to 133 °C that are in linear proportion to the content of CHO-PA in the polymer backbone. The Poly(PO-CHO-PA) shows superior thermal stability and is feasible for melt processing. The Poly(PO-CHO-PA) exhibits high tensile strength and excellent barrier properties because of its aromatic moiety containing. The similar performances with PS make these new semi-aromatic polyesters promising for potential applications in packaging materials, especially for foaming and illumination equipment materials.

**ACKNOWLEDGMENTS**

This work was financially supported by the National Natural Science Foundation of China (No. 51673131) and the
Fundamental Research Funds for the Central Universities (No. 171GJC37).

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