One pot synthesis and characterization of novel poly(ether ester) multiblock copolymers containing poly(tetramethylene oxide) and poly(ethylene terephthalate)†

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We demonstrate here a novel method to synthesize poly(ethylene terephthalate)-block-poly(tetramethylene oxide) multiblock copolymers (PET-b-PTMO-b-PET), by the one pot melt polymerization of cyclic oligo(ethylene terephthalate)s (COETs) using poly(tetramethylene oxide) (PTMO) as a macrorinitiator. Two-dimensional and one-dimensional nuclear magnetic resonance (2D and 1D-NMR) techniques, including 1H–13C Heteronuclear Single Quantum Coherence (HSQC) and 1H–1H Correlation Spectroscopy (COSY), have been used to characterize and reveal the multiblock copolymer structures and absolute molecular weights. It was found that the COETs were consumed completely within 15 minutes, and the molecular weights of the block copolymers increased linearly with reaction time. Based on the polymerization kinetic studies, a two-stage polymerization mechanism is proposed: the ring-opening polymerization of COETs by a PTMO macroinitiator to PET-b-PTMO-b-PET triblock copolymers at the first stage, followed by the in situ condensation polymerization of triblock copolymers to (PET-b-PTMO-b-PET) multiblock copolymers at the second stage. The structures of the multiblock copolymers are further characterized and confirmed by viscometry and gel permeation chromatography (GPC). These multiblock copolymers show improved thermal stability when compared to PTMO homopolymers, and double crystalline properties from PTMO and PET segments, as revealed by thermogravimetric analysis and differential scanning calorimetry, respectively.

1. Introduction

Poly(ether ester) copolymers are a kind of rod-coil block copolymer, where the soft segments consist of polyethers while the hard segments consist of crystalline polyesters, which attract great interest because they possess various excellent properties, such as good mechanical properties, toughness, chemical resistance, excellent surface appearance, and are used as high performance materials.1–7 To improve the mechanical properties, the hard segments are usually crystalline aromatic polyesters, like poly(butylene terephthalate) (PBT),8–12 poly(ethylene terephthalate) (PET),13 poly(butylene 2,6-naphthalene dicarboxylate), etc.14,15 The soft segments most frequently used are poly(tetramethylene oxide)s (PTMOs, also known as poly(tetrahydrofuran)s or PTHFs). Normally, poly(ether ester) copolymers are synthesized by condensation polymerization of relatively low molecular weight dihydroxyl terminated polyethers with polyester monomers at high temperatures.16–20 This process produces random multiblock copolymers with polyester homopolymers coexisted and has some drawbacks, e.g., the molecular weights and structures of the hard polyester segments are uncontrollable, the total molecular weights of the polymers are not too high, and they require high vacuum to remove the produced alcohols.21

It is well-known that poly(ethylene terephthalate)s (PETs) have valuable characteristics including strength, toughness, solvent resistance, and heat resistance. Traditionally, PETs were synthesized by condensation polymerization, until Brunelle et al. reported the synthesis of cyclic oligo(ethylene terephthalate)s (COETs), and the ring-opening polymerization (ROP) of COETs to PETs.22–24 Since there is no byproduct produced during the polymerization process, and the polymerization speed is quite fast, PET with high molecular weights can be synthesized within 15 min.24 Besides the above merits, this method has also attracted great interest because of the low melt viscosities and melting
temperatures of cyclic oligomers,\textsuperscript{24,25} which are enough for these melts to be applied in processes such as reaction injection molding and composite reaction injection molding. However, to our knowledge, despite the relatively abundant studies on the ROP of cyclic oligo( aromatic ester)s, there is no report on the synthesis of PET-based poly(ether ester)s by ROP of COETs.

Based on the ROP mechanism of COETs, we believe that the melt ROP of COETs by dihydroxyl terminated polyethers would produce PET-\textit{block}-polyether-\textit{block}-PET triblock copolymers. In the current work, PTMO was selected as the polyether soft segment. Because the melting temperature of COET mixture is about 265 °C,\textsuperscript{24} it is possible that condensation polymerization and transesterification reactions occur at this high temperature. As a result, multiblock copolymers can be obtained. To follow the reaction mechanism, we developed an improved quantitative \textsuperscript{1}H NMR characterization technique, where the coupling of \textsuperscript{13}C to \textsuperscript{1}H was suppressed, a much longer relaxation delay time was selected (20 s, \textasciitilde10 times of T1), and the signals were taken at PW90 to ensure maximum signal acquisition. The block copolymer molecular weights and compositions can be revealed by chain end and functional groups analysis, and the polymerization kinetics were studied. This NMR characterization method works well even when the total molecular weights of polymer reached $10^5$ g mol\textsuperscript{-1}, and gel permeation chromatography (GPC) analysis and viscosity measurements were used to verify the results.

### 2. Experimental

#### 2.1. Materials

Chloroform (CHCl\textsubscript{3}), dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}), tetrahydrofuran (THF), triethylamine (Et\textsubscript{3}N), ethylene glycol (EG) and ammonium hydroxide were purchased from Qiangsheng Chemical of Suzhou, China. Terephthaloyl chloride (TPC) (Alfa Aesar, 99%) was recrystallized from hexane three times. Dihydroxyl terminated PTMO ($M_n = 2900$ g mol\textsuperscript{-1}, Sigma-Aldrich) and titanium tetrabutoxide (Ti(n-C\textsubscript{4}H\textsubscript{9}O)\textsubscript{4}, Alfa Aesar, 98%) were used as received. EG, Et\textsubscript{3}N and CH\textsubscript{2}Cl\textsubscript{2} were refluxed over CaH\textsubscript{2} and distilled before use. THF was refluxed over Na and distilled before use. 1,4-Diazabicyclo[2.2.2]-octane (DABCO) (Acros, 99%) was sublimed before the reaction.

![Scheme 1](image-url)

**Scheme 1.** The one pot synthetic route to (PET-\textit{b}-PTMO-\textit{b}-PET\textsubscript{x}) multiblock copolymers: (1) ring-opening polymerization of COETs with PTMO to PET-\textit{b}-PTMO-\textit{b}-PET triblock copolymers; (2) condensation polymerization of block copolymers to multiblock copolymers, and (3) transesterification reactions between multiblock copolymers.
2.2. Synthesis of cyclic oligo(ethylene terephthalate) (COETs)

COETs were synthesized using a similar procedure as described in ref. 22 and 23, using terephthaloyl chloride (TPC) and ethylene glycol (EG) under pseudo high dilution conditions in dichloromethane with 1,4-diazabicyclo[2.2.2]-octane (DABCO) as a catalyst. Yield: 35%. 1H NMR (400 MHz, CDCl3), δ (ppm): 4.69 (4H, t), 8.08–8.10 (4H, d).

2.3. One pot synthesis of (PET-b-PTMO-b-PET)ₙ multiblock copolymers

Scheme 1 represents the synthesis of the poly(ether ester) multiblock copolymers. The predetermined amount of COETs and PTMO (Mₙ = 2900 g mol⁻¹) was placed in a 100 mL three-necked flask equipped with a mechanical stirrer under the nitrogen atmosphere. The mixture was heated to 270 °C for 5 min, after which titanium tetrabutoxide was added to start the polymerization. After the predetermined polymerization time, the reaction mixture was cooled to room temperature quickly and characterized without further purification.

2.4. Characterization

The gel permeation chromatography (GPC) experiments were performed on a modular system comprising a Waters 1515 pump, Waters 717 plus autosampler, and 2414 refractive index detector with three 300 mm (length) columns with a particle size of 5 µm (PL gel mixed-C, Polymer Laboratories). THF was used as an eluent at a flow rate of 1.0 mL min⁻¹. Calibration was made against standard monodisperse linear polystyrenes. The solution viscosities of the polymers (c = 20 mg mL⁻¹) were examined by using a SNB-3 digital viscometer (Shanghai Nirum Intelligent Technology Co, Ltd.) in phenol–tetrachloroethane (1:1 in mass) mixture solvents. The NMR spectra were recorded at room temperature on the Varian 400 MHz INOVA instrument using the CF₃COOD/CDCl₃ (1/10 in volume) mixture solvent with tetramethylsilane (TMS) as the internal reference. Thermogravimetric analysis (TGA) was performed with a heating rate of 10 °C min⁻¹ from room temperature to 800 °C under a continuous nitrogen flow rate of 50 mL min⁻¹ with an SDT-2960TG/DTA TA instrument. The temperature of thermal degradation (Tₙ) was measured at the point of 5% weight loss relating to the weight at room temperature. Differential scanning calorimetry (DSC) was carried out on the TA Q200 instrument under a nitrogen atmosphere in the temperature range from −50 °C to 300 °C at heating and cooling rates of 10 °C min⁻¹. The first cooling and the second heating scans were used to determine the melting and crystallization peaks.

3. Results and discussion

The determination of molecular weights and structures of polymers is always the key for polymer scientists. This is very difficult for those polymers with high polarity like polyesters and polyamides, since it is hard to find a proper solvent for GPC characterization and usually viscosity measurements are used instead, which give relative molecular weights. Recently, with the progress of ¹H NMR techniques, the determination of the number-average molecular weights of polymers by the chain-end estimation method using ¹H NMR is well-established and works well with polymers with small molecular weights of several thousand Daltons.²⁶–³⁰

However, due to the couplings of ¹³C to ¹H, which take about 1% integrated peak area from those major peaks of ¹H connected with ¹²C, the error is bigger for polymers with molecular weights higher than 10⁴.³¹ On the other hand, since the relaxation time of protons at the chain end and on the backbone is different, the NMR signals would be suppressed if the relaxation delay provided at the front of each acquisition scan was not long enough. Normally the chain-end protons have longer relaxation time than those on the backbone, which makes their peak integration value smaller due to the shortage of the NMR relaxation time, and results in higher calculated molecular weights. To determine the molecular weights of the whole polymer and the number of segments in our multiblock copolymers, we used an improved quantitative ¹H NMR method, where the decoupling of ¹³C to ¹H was applied during acquisition, with the delay time (20 s) set as 10 times the relaxation time (T₁), and the experiments were conducted at 90° pulse for the maximum signal acquisition.

The method was applied first to estimate the number average molecular weights of PTMO. The average repeating units in PTMO can be calculated from the ratio of the integral value of methylene groups at the chain end (CH₂OH, peak e) to the total methylene groups (CH₂O, peak h). The calculated value is 43.0, which is corresponding to the number average molecular weight of 3100 g mol⁻¹. This value is very close to the molecular weight provided by the producer (2900 g mol⁻¹), indicating the accuracy of our NMR acquisition method.³²

Fig. 1 represents the ¹H 1D-NMR curves of P1 samples (reacted at 270 °C with mₚTMO/mₚCOETs = 3/1 and 0.075 wt% Ti(n-C₄H₉O)₄) after polymerization for different times, with the corresponding peak assignments at the top of the figure. The detailed list of integration values for all peaks can be found in the ESI (Table S1†). It was found that after polymerization for 15 minutes, the peak at the chemical shift of 3.65 ppm and 4.82 ppm disappeared. The peak at 3.65 ppm is corresponding to the methylene hydrogen of the functional end groups (CH₂–OH) from PTMO, while the peak at 4.82 ppm to COETs, respectively. On the other hand, peaks at positions of 4.42 ppm, 4.16 ppm and 4.60 ppm appeared. The peak at 4.42 ppm is corresponding to the PTMO’s methylene protons at the chemical position e, which is linked to PET segments by an ester bond, while the other two corresponding to the PET’s methylene protons at the polymer chain end at positions a and b, respectively, as listed in Fig. 1. These results reveal that all the end groups of PTMO were reacted with COETs, and all the COETs are consumed, indicating that the ROP of COETs by PTMO is rapid and finished within 15 minutes.

The assignment of the peaks in the ¹H NMR figure is deduced and supported by the 2D-NMR characterization. Fig. 2A shows the ²H–¹H HSQC full spectra of the copolymer P1-1 from which selected regions are expanded and shown in Fig. 2B–D. In phase-sensitive HSQC spectra, signals coming from methyl (CH₃) and methine (CH) groups stay in the same
phase, while signals indicating methylene (CH2) groups show up at the opposite phase. For example, in Fig. 2C and D we see methylene groups in warm colors while in Fig. 2B methine from the phenyl groups of copolymer P1-1 are blue. Fig. 2D represents the middle methylene groups from PTMO segments with no oxygen attached (-OCH2CH2CH2CH2O-). In Fig. 2C methylene groups appear at the regions of δ13C = 59–70 ppm and δ1H = 3.6–4.8 ppm, downfield shifted from the normal CH2, which indicates they are connected with an electron-drawing group like oxygen or fluorine. In this case, peaks a, b, d, e and h can be assigned as the CH2O methylene groups. From the height and integration values, we can clearly distinguish the main peaks d (PET)s and g, h (PTMO’s) from the minor peaks of a, b, e and f, which are either from the PTMO segment ends connected with PET or copolymer chain end groups.

Fig. 3A shows the 1H-1H COSY full spectra of copolymer P1-1, with the selected region expanded into Fig. 3B. Intensive cross-peaks observed between h and g indicate that these two methylene groups connected to each other are from PTMO segments (-OCH2(g)-CH2(g)-CH2(g)-CH2(h)O-). Similarly, the cross-peak between e and f proves that they belong to the PTMO segments’ end linked with PET (COO-CH2(e)-CH2(f)-CH2(g)-CH2(h)O-), while a and b cross-peaks describe the chain end structure (-OCH2(a)-CH2(b)O-). Together with the HSQC and 1H NMR data, the formation of multiblock copolymers is proved and the structure assignments are presented in the top of Fig. 1.

In 1H 1D-NMR, since peak b (δ = 4.60 ppm) is slightly overlapped with peak d (δ = 4.78 ppm) and peak e (δ = 4.42 ppm), peak a (δ = 4.16 ppm) was used as a chain end proton for polymer structure estimation. The total repeating units of ET (N_{ET}) and TMO (N_{TMO}) in copolymers can be calculated by the integration ratio of chain end to corresponding repeating units by 1H NMR spectra, using the following equation:

\[
\frac{I_a}{I_d} = \frac{4}{4N_{ET} - 8}
\]

where \(I_a\), \(I_d\), \(I_e\) and \(I_h\) are the integration values for the corresponding peak at positions a, d, e and h, and \(N_{ET}\) and \(N_{TMO}\) are the total repeating units of ET and TMO, respectively. The total number-average molecular weights of the whole polymer (\(M_n\)) can thus be calculated by \(M_n/Dalton = \frac{72.0 \times N_{TMO} + 192 \times N_{ET}}{72.0 + 192}\) (where 72.0 and 192 were the molecular weights of the repeating units of PTMO and PET chains), with the results listed in Table 1.

Table 1 clearly shows that the total molecular weights of the polymers increased with the reaction time as the total repeating units of ET \(N_{ET}\) and TMO \(N_{TMO}\) increase. Since COETs were consumed within 15 minutes, the increase of the total copolymer molecular weights after that is not from ROP, but from the condensation polymerization between block copolymers.

As mentioned above, peak e in the NMR figure can be assigned to the methylene end group of PTMO linked with PET by an ester bond. The average repeating units of TMO \(S_{TMO}\) and ET \(S_{ET}\) in each corresponding segment can be calculated by the following equation:

\[
\frac{I_e}{I_e + I_h} = \frac{4}{4S_{TMO}}
\]

The calculated values are listed in Table 1. The results show that the average repeating units of TMO and ET in corresponding PTMO or PET segments do not change with increasing reaction time. Considering the fact that the total molecular weights of the polymers increased with reaction time,
these results demonstrate that condensation polymerization occurred at these studied stages between block copolymers, where ethylene glycol was released from the reaction mixture with the corresponding multiblock copolymers formed, i.e., the one pot polymerization process contains two stages: the ring opening polymerization of COETs by a PTMO macroinitiator to PET-b-PTMO-b-PET triblock copolymers at the first stage, followed by the condensation polymerization of triblock copolymers to multiblock copolymers at the second stage, as illustrated in Scheme 1. The mechanism is supported by the observation of ethylene glycol small droplets at the nitrogen outlet part. Since there is only one feeding step required for this two-stage polymerization process, this polymerization technique can be looked as a one pot one feeding step process with two polymerization stages.

To further prove the mechanism proposed in Scheme 1, the PET-b-PTMO-b-PET triblock copolymer intermediates need to be confirmed. However, the in situ polymerization of triblock copolymers to multiblock copolymers is so rapid that pure triblock copolymers are hard to be obtained, as NMR characterizations reveal that multiblock copolymers are formed within 5 minutes. Based on the reaction mechanism in Scheme 1, triblock copolymers can be obtained if the release of ethylene glycol in stage 2 is hindered. In a controlled experiment, COETs, PTMO \( m_{\text{PTMO}}/m_{\text{COETs}} = 3/1 \) and \( \text{Ti}(n-C_4H_9O)_4 \) were mixed together and hot-pressed at 270 °C under a 10 MPa pressure for 90 minutes, after which PTMO and COETs were completely consumed. Similar to multiblock copolymers, the polymer chain end groups and block copolymer structures can be assigned from the quantitative \(^1\text{H} \) 1D-NMR spectra (see ESI, 

Fig. 2  Two dimensional \(^1\text{H}–^{13}\text{C} \) HSQC spectra of (PET-b-PTMO-b-PET)_x multiblock copolymer P1-1, with the whole spectra (A), and selected correlated regions (B–D). Solvent: CF₃COOD/CDCl₃ (1/10 in volume); concentration: 0.02 g mL⁻¹.

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Fig. S1† and 1H–13C HSQC 2D-NMR experiments (Fig. S2†). The structure of copolymers is revealed to be PET-b-PTMO-b-PET triblock copolymers, since the ratio of the methylene peak integration value for the chain end (peak a or b) to polyether–ester linkage (peak e) is 1 : 1. The proposed mechanism in Scheme 1 is greatly supported by these results.

It should be noted that at this high polymerization temperature, transesterification reactions may occur, as reported by Burch et al.34 The mechanism is illustrated in Scheme 1 (stage 3). However, this transesterification between the multiblock copolymers will not affect the average molecular weights of the total block copolymers, nor the average molecular weights of each segments. On the other hand, no PET homopolymer was observed, as all the block copolymers formed can be dissolved in THF at 60 °C, which is a bad solvent for PET.

Since there are only PET’s chain end groups observed while no PTMO’s chain end groups are observed from NMR, the structure of multiblock copolymer can be assigned as (PET-b-PTMO-b-PET)\(_x\) (or PET-b-[PTMO-b-PET])\(_x\). This also follows the polymerization mechanism where PET-b-PTMO-b-PET triblock copolymers are formed first by ROP of COETs by the PTMO macroinitiator. The average repeating number of PET-b-PTMO-b-PET block segments, \(x\), can be calculated by the following equation:

\[
\frac{I_e}{I_a} = \frac{4x}{4}
\]

The calculated \(x\) values at different polymerization times are listed in Table 1. These results show the number of block segments increased with reaction time. When reacted for 15 minutes, a mixture of pentablock copolymers and heptablock copolymers was formed on an average as the \(x\) value is 2.41, while multiblock copolymers with larger \(x\) formed with the increasing reaction time.

![Fig. 3 Two dimensional 1H–1H COSY spectra of (PET-b-PTMO-b-PET)\(_x\) multiblock copolymer P1-1, with the whole spectra (A), and selected correlated regions (B). The colored squares indicate the correlations between neighboring groups. Solvent: CF\(_3\)COOD/CDCl\(_3\) (1/10 in volume); concentration: 0.02 g mL\(^{-1}\).](image)

Table 1 The integration value of peaks by 1H NMR for the PTMO macroinitiator and multiblock copolymers synthesized with different reaction times and the corresponding structures calculated\(^a\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction time (min)</th>
<th>a</th>
<th>e</th>
<th>h</th>
<th>d</th>
<th>(N_{\text{TMO}})</th>
<th>(N_{\text{ET}})</th>
<th>(S_{\text{TMO}})</th>
<th>(S_{\text{ET}})</th>
<th>(x)</th>
<th>(M_n) (kg mol(^{-1}))</th>
<th>(M_{n,GPC}) (kg mol(^{-1}))</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTMO</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>43.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>3.10</td>
<td>6.64</td>
<td>1.77</td>
</tr>
<tr>
<td>P1-1</td>
<td>15</td>
<td>4.00</td>
<td>9.65</td>
<td>408</td>
<td>35.1</td>
<td>104</td>
<td>8.78</td>
<td>43.3</td>
<td>3.64</td>
<td>2.41</td>
<td>9.17</td>
<td>14.1</td>
<td>1.61</td>
</tr>
<tr>
<td>P1-2</td>
<td>30</td>
<td>4.00</td>
<td>19.7</td>
<td>847</td>
<td>72.2</td>
<td>217</td>
<td>18.1</td>
<td>44.0</td>
<td>3.66</td>
<td>4.93</td>
<td>19.1</td>
<td>17.5</td>
<td>1.71</td>
</tr>
<tr>
<td>P1-3</td>
<td>45</td>
<td>4.00</td>
<td>35.7</td>
<td>1490</td>
<td>132</td>
<td>381</td>
<td>33.0</td>
<td>42.7</td>
<td>3.70</td>
<td>8.93</td>
<td>33.8</td>
<td>21.5</td>
<td>1.72</td>
</tr>
<tr>
<td>P1-4</td>
<td>60</td>
<td>4.00</td>
<td>52.9</td>
<td>2210</td>
<td>200</td>
<td>566</td>
<td>50.0</td>
<td>42.8</td>
<td>3.78</td>
<td>13.2</td>
<td>50.4</td>
<td>26.1</td>
<td>1.69</td>
</tr>
<tr>
<td>P1-5</td>
<td>90</td>
<td>4.00</td>
<td>94.1</td>
<td>3890</td>
<td>354</td>
<td>996</td>
<td>88.5</td>
<td>42.3</td>
<td>3.76</td>
<td>23.5</td>
<td>88.7</td>
<td>31.8</td>
<td>1.75</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: \(m_{\text{PTMO}}/m_{\text{COETs}} = 3/1\) with 0.075 wt% Ti(\(\eta\)-C\(_5\)H\(_4\)O\(_4\))\(_4\) at 270 °C. \(N_{\text{TMO}}, N_{\text{ET}}, S_{\text{TMO}}, S_{\text{ET}}\) in corresponding polymer segments, respectively. \(x\) is the repeating units of (PET-b-PTMO-b-PET)\(_x\) segments in (PET-b-PTMO-b-PET)\(_x\) multiblock copolymers. \(M_n\): number-average molecular weights of polymer by means of NMR. \(M_{n,GPC}\): number-average molecular weights of polymers in THF by means of GPC.
The influence of the catalyst amount, reaction temperature and polymerization time on the copolymer structure is studied, and the results are presented in the ESI† (Table S1 for P1 copolymer series with 0.075 wt% catalyst amount at 270 °C, Fig. S3 and Table S2† for P2 copolymer series with 0.15 wt% catalyst amount at 270 °C, Fig. S4 and Table S3† for P3 copolymer series with 0.075 wt% catalyst amount at 280 °C). The average repeating units of TMO (N_{TMO}) and ET (N_{ET}) in each corresponding segments are almost the same regardless of the reaction time, catalyst amount, and reaction temperature, following well with our proposed condensation polymerization mechanism.

The total repeating units of ET (N_{ET}) and TMO (N_{TMO}) in copolymers, and the total number average molecular weights (M_n) of the polymers, increased with reaction time, as presented in Tables 1, S2 and S3. However, with the same reaction time, N_{ET}, N_{TMO}, and M_n of (PET-b-PTMO-b-PET)_x multiblock copolymers are slightly larger with higher catalyst amount and polymerization temperature in our studied region. After reacting for 90 minutes, the molecular weights of the multiblock copolymers are higher than 90 000 g mol⁻¹, which are very difficult to be achieved by traditional condensation polymerizations. It should also be noted that our polymerization process can be carried out under normal conditions via a one pot one feeding step process without the need for high vacuum, which provides a good synthetic route to poly(ether ester) multiblock copolymers.

The condensation polymerization of PET-b-PTMO-b-PET triblock copolymers to form (PET-b-PTMO-b-PET)_x multiblock copolymers can be looked upon as an AB type monomer based condensation polymerization process. From this, we can have the following equation to describe the reaction kinetics:

\[ X_n = k't + 1 \]

where \( X_n \) is the average degree of polymerization for the AB-type monomer based condensation polymerization, \( t \) is the reaction time, \( k' \) is the constant for a given condition which is related to the starting functional group concentration, catalyst concentration, polymerization reaction constant and temperature. The detailed deduction of eqn (6) can be found in the ESL.†

The degree of polymerization, \( X_n \), can be calculated by NMR and is the same as repeating units of triblock copolymers (x) in (PET-b-PTMO-b-PET), multiblock copolymers. Clearly, the degree of polymerization increases linearly with reaction time, as shown in Fig. 4. The well-fitted linear fitting lines for data at different reaction times with 0.075 wt% and 0.15 wt% catalyst amount at 270 °C, and 0.075 wt% catalyst amount at 280 °C, indicate that the polymerization mechanism follows eqn (6), which is deduced from the condensation polymerization mechanism proposed in Scheme 1. The slopes for the linear fitting curves are 0.285 min⁻¹ for the reaction with 0.075 wt% catalyst at 270 °C, 0.316 min⁻¹ for 0.15 wt% catalyst at 270 °C, and 0.308 min⁻¹ for 0.075 wt% catalyst at 280 °C, respectively. It shows that the degree of polymerization increased slightly with the increased catalyst concentration or temperature.

The intercept of linear fitting curves to \( X_n = 1 \) is 14.4 minutes for polymerization carried out at 270 °C with 0.075 wt% catalyst amount, and 13.6 minutes for 0.15 wt% catalyst amount. This is the average time that ROP of COETs by PTMO finishes, and the condensation polymerization starts. The similar value for the above two conditions indicates that the ROP is not affected much by the catalyst amount. For polymerization carried out at 280 °C with 0.075 wt% catalyst amount, the intercept of linear fitting curves to \( X_n = 1 \) is 11.5 minutes. Compared to the value obtained at 270 °C, this value is much smaller, which indicates that the first stage of the ROP process is more sensitive to the temperature than the catalyst amount.

The viscosity measurements of the corresponding polymers were carried out to demonstrate the reliability of our results from NMR measurements. Since the concentration of the polymers, the solvent composition and the experimental temperature are the same, a higher measured apparent viscosity indicates higher molecular weights. Fig. 5 shows the viscosity measured for P1 samples with different reaction times. Clearly, the viscosity increased with the reaction time, coincides well with the results from NMR data.

Fig. 6 shows the GPC curves of P1 series samples reacted at different times \((m_{PTMO}/m_{COETs} = 3/1, 0.075\text{ wt\% catalyst amount, polymerized at 270 °C})\), and the results are summarized in Table 1. The curves show that the related molecular weights of block copolymers increased with polymerization time, in agreement with the results from NMR data. The polydispersity of the main peak is around 1.7 for all the polymers. It should be noted that for copolymers P1-3 and P1-5, there is a shoulder peak (at about 17 minutes) appeared with much shorter retention time, and the peak value moved to the left side with the increasing multiblock length. This high molecular weight portion is probably due to the self-assembly of multiblock copolymers to form micelles in THF, since the solution becomes cloudy and the filtration of the solution by a 0.45 μm filter is not easy. As all the (PET-b-PTMO-b-PET), multiblock copolymers have the same PET and PTMO segment lengths, but
just different repeating numbers of \( x \), our results demonstrate that it also affects the self-assembly of the multiblock copolymers. Detailed studies on the influence of multiblock copolymer compositions on their self-assembly properties are under current investigation.

To test the reliability of this one pot polymerization technique, \((\text{PET-b-PTMO-b-PET})_x\) multiblock copolymers with different PTMO contents were synthesized using the similar polymerization conditions. Fig. 7 shows the quantitative \(^1\text{H} \) NMR curves of these multiblock copolymers, and the results are summarized in Table 2. Copolymers P4-6 were all synthesized at 270 °C for 15 min using 0.075 wt% catalyst amount. It shows that this one pot polymerization technique works well for the synthesis of block copolymers with PTMO contents ranging from 50 wt% to 80 wt%.

With the same reaction time, \( x \), the degree of polymerization of the \((\text{PET-b-PTMO-b-PET})_x\) segment, increased with the PTMO feeding ratio. This is reasonable since the concentration of end groups increased with the higher PTMO content and the condensation polymerization between block copolymers is more rapid. The contents of each block in multiblock copolymers are close to the feeding ratio, indicating the easy control of this technique on the final copolymer composition and the versatile application in the multiblock copolymer synthesis.

The thermal stability of these multiblock copolymers with different PTMO contents was studied by TGA and the results are listed in Table 2. Fig. 8 shows the TGA curves of the multiblock copolymers and the corresponding precursor of the PTMO macroinitiator and COETs. The multiblock copolymers have similar thermal stability with 5% weight loss at a temperature around 345 °C, similar to the PET homopolymers,\(^{24}\) which are much better than PTMO homopolymers. The improved thermal stability of multiblock copolymers than PTMO homopolymers indicates that the decomposition of PTMO can be hindered by coupling the chain end with functional groups of better thermal stability. This is supported by the observation of only one decomposition stage, contrary to other block copolymer systems where two decomposition stages were observed.\(^{35-38}\) These results support the formation of multiblock copolymers (not blends), and the improvement of PTMO’s thermal stability will be useful for their applications.

Fig. 9 shows the DSC curves of \((\text{PET-b-PTMO-b-PET})_x\) multiblock copolymers with different PTMO contents, with the results summarized in Table 2. All the copolymers show a crystal melting peak at around 23 °C during heating, corresponding to the melting peak of PTMO crystals, with the crystallization peak at around –10 °C during the cooling process.
respectively. The PET melting peak was also observed for copolymers P5 and P6 at about 250 °C, similar to commercially available PET homopolymers. For copolymer P4, the melting peak of PET is not obvious and only a small bump was observed with the temperature much lower than the others. This is due to the different PET segment average lengths in multiblock copolymers, which can be deduced roughly by the total repeating units of ET in multiblock copolymer over trilob copolymer segment repeating units \(\{N_{ET} / n\}\). The calculated values are 2.7, 6.1 and 12 for P4, P5, and P6, respectively. For copolymer P4, the average repeating length of PET in segments is too small to form crystals. The above phenomena indicate that these multiblock copolymers are double crystalline polymers, which may have potential applications in shape memory materials.

4. Conclusions

\((PET-b-PTMO-b-PET)_{x}\) multiblock copolymers were synthesized by a one pot one step melt polymerization process using COETs as monomers, PTMO as a macroinitiator, and Ti\((n-C_4H_9O)\)\(_4\) as a catalyst. 2D-HSQC, COSY and 1D-quantitative \(^1\)H NMR experiments have been carried out to reveal the structure of multiblock copolymers. It was found that the average total repeating units of TMO \((N_{TMO})\) and ET \((N_{ET})\) in copolymers, and the total block copolymer molecular weights increase linearly with the reaction time, while the average repeating units of TMO \((S_{TMO})\) and ET \((S_{ET})\) in the corresponding block segment remain unchanged. Investigation on the polymerization kinetics reveals that the formation of multiblock copolymers consists of two stages: the ring-opening polymerization of COETs by a PTMO macroinitiator to PET-b-PTMO-b-PET triblock copolymers at the first stage and the condensation polymerization of the triblock copolymers to \((PET-b-PTMO-b-PET)_{x}\) multiblock copolymers at the second stage. The polymerization speed is slightly affected and increased with the catalyst content and reaction temperature. The multiblock copolymers show much better thermal stability than PTMO homopolymers, and double crystalline properties from PTMO and PET segments, as revealed by TGA and DSC experiments. Our polymerization method affords a facile way to synthesize poly(ether ester) multiblock copolymers with a well-defined structure and potential applications as advanced materials.

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**Notes and references**

33. To verify the accuracy of this technique, a polystyrene sample with a functional chain end was measured by GPC calibrated by standard PS, normal 1H NMR technique and our quantitative 1H NMR technique. The number average molecular weights are 3170 g mol⁻¹ from GPC, 3560 g mol⁻¹ from normal setting 1H NMR, and 3160 g mol⁻¹ from quantitative 1H NMR.