

Synthesis of Poly(butylene terephthalate)-Poly(tetramethylene glycol) Copolymers Using Terephthalic Acid as Starting Material: A Comparison between Two Synthetic Strategies^{*}

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Abstract Poly(butylene terephthalate)-poly(tetramethylene glycol) (PBT-PTMG) copolymer is prepared with terephthalic acid (PTA) rather than its dimethyl ester (DMT) as starting material by a two-step melt polycondensation. This process includes the synthesis of PBT prepolymer from PTA with 1,4-butanediol (BDO) in the first step, followed by the synthesis of PBT-PTMG copolymer from PBT prepolymer with PTMG in the second step. The molecular weight, composition as well as thermal and mechanical properties of the products from the two-step melt polycondensation are compared with the properties of the PBT-PTMG from the traditional one-step melt polycondensation. When the PTMG content is low, there is only slight difference in molecular weight, composition, thermal and mechanical properties among PBT-PTMG copolymers obtained from these two methods. However, when the PTMG content is high, only the two-step strategy is able to give high molecular weight products, and the products have comparable thermal and mechanical properties with those from traditional one-step strategy using DMT as starting material.

Keywords: Polycondensation; Elastomer; Poly(ether-esters).

INTRODUCTION

Poly(butylene terephthalate)-poly(tetramethylene glycol) (PBT-PTMG) copolymer is one of the most important thermoplastic poly(ether ester) elastomers (TPEEs) in the market, which was firstly commercialized under the trademark “Hytrel” in 1972^[1, 2]. The excellent mechanical and thermal properties of PBT-PTMG copolymer arise from its unique two-phase domain structure employing PBT as hard segment forming crystalline region and PTMG as soft segment forming amorphous region^[3–5].

TPEEs including PBT-PTMG as well as poly(ethylene terephthalate)-poly(ethylene glycol) (PET-PEG)^[6], and PBT-PEG^[7, 8] are prepared by either a one-step^[9–12] or a two-step^[13–15] melt polycondensation process using dimethyl terephthalate (DMT) as the starting material. Co-monomer can be added to tune the property of TPEEs by changing the hard segment composition. For example, succinic acid is used to increase the biodegradability of TPEEs such as PBT-PBS-PTMG^[16] and PBT-PBS-PEG^[9]. Si-containing TPEEs can be synthesized by adding organosilicon monomers such as 1,1,3,3-tetramethyl-1,3-bis(*p*-carbomethoxyphenyl) disiloxane or dimethyl bis(*p*-carbomethoxyphenyl) silane, resulting in increase of the hydrophobicity, heat resistance as well as gas

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permeability of O₂ and N₂ of the copolymer^[17, 18]. In these examples, DMT is used as starting material other than PTA. The process includes a transesterification reaction between DMT with diol and polyether under nitrogen at about 200 °C and subsequently a polycondensation reaction under higher temperature and reduced pressure. Since the first TPEE was developed by Coleman in 1954^[19], DMT other than terephthalic acid (PTA) was involved in this process, because DMT was widely used as the starting material for the synthesis of polyesters as well as TPEEs at the time when high-purified PTA was unavailable. With the development on the synthesis and purification technologies of PTA, it is now the major starting material for the synthesis of polyesters. However, for the synthesis of TPEEs, there is few report in the literature using PTA as starting material^[20]. In comparison with DMT, PTA has several advantages for the synthesis of polyesters and TPEEs, 1) the price of PTA is lower than that of DMT, 2) water other than methanol is distilled in the reaction. Therefore, PTA route is a more cost-effective and safer process than the DMT one.

However, simply replacing DMT with PTA for the synthesis of TPEEs using one-step melt polycondensation has huge problems. In the PTA route, an esterification reaction takes place between PTA and diol and polyether, rather than a transesterification reaction in the case of one-step DMT route. The esterification between PTA and diol will be impacted due to the present of polyether because of its low reactivity of terminal hydroxyl groups, especially when large amount of polyether presents. Many efforts have been devoted to avoid the influence of polyether on the esterification of PTA with diol in the synthesis of TPEEs^[21–23]. For instance, Huang and coworkers^[23] prepared cyclic oligo(ethylene terephthalate)s (COETs) and then use one-pot melt polymerization with PTMG to synthesize poly(ether ester) multiblock copolymer, in which PTMG played a very interesting role as a macroinitiator for the ring-opening polymerization (ROP) of COETs to pursue the high reactivity. However, many methods can avoid the adverse effects of PTMG during esterification between PTA and diol, it could not fit for the large-scale application in the synthesis of TPEEs.

Therefore, in this work, we use both one-step and two-step strategies for the synthesis of PBT-PTMG copolymer with PTA as starting material instead of DMT and evaluate the influence of synthetic strategies on the properties of PBT-PTMG. For the one-step strategy, all reactants are added at one time, while for the two-step one, instead of feeding PTMG together with PTA and BDO in one-step, we first carry out the synthesis of PBT prepolymer from PTA and BDO in the first step, and then feed the PTMG in the second step, after which the polycondensation reaction between PBT prepolymer and PTMG continued to get high molecular weight product. This two-step strategy effectively avoids the influence of polyether on the esterification of PTA with BDO. Characterizations including nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) as well as tensile test are provided to show the properties of the PBT-PTMG copolymers. Accordingly, the advantages of the two-step strategy of the TPEEs are also discussed in comparison with the one-step one.

EXPERIMENTAL

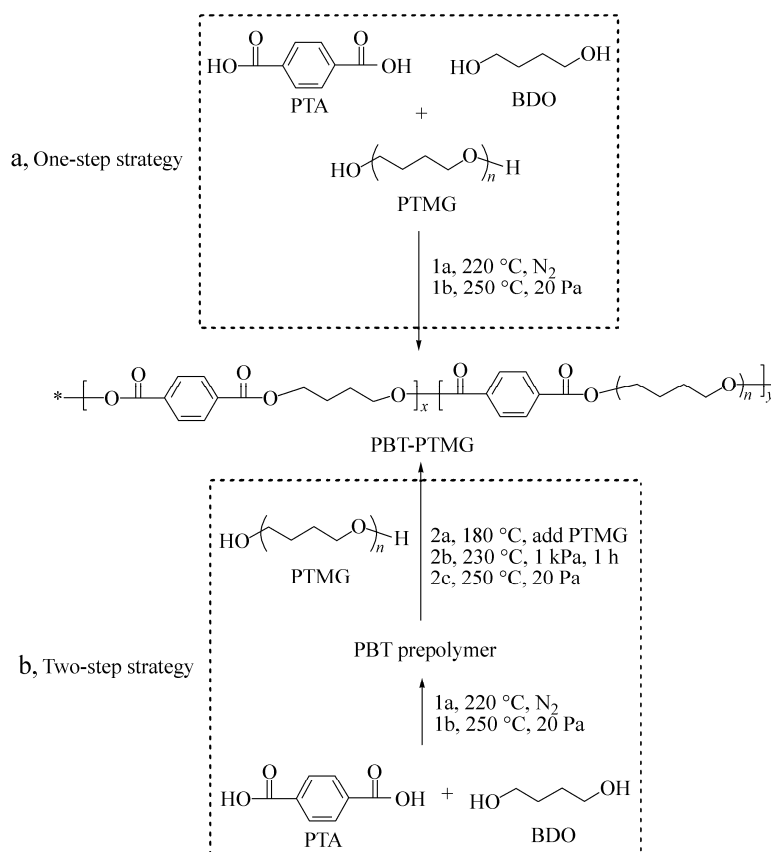
Materials

PTA, BDO, PTMG with M_n of 1000 and 2000 g/mol, titanium(IV) butoxide and antioxidant1010 were all purchased from Aladdin Reagent Co. Ltd (Shanghai, China). Chloroform, trifluoroacetic acid, phenol, tetrachloroethane and 2-chlorophenol were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All the chemicals are used as received without further treatment.

Synthesis of PBT-PTMG

We prepared the PBT-PTMG copolymers by melt polycondensation technique with PTA as starting material. More importantly, for the feeding of PTMG, two different strategies were used, addition of PTMG together with PTA and BDO at the beginning of the reaction (one-step strategy), and addition of PTMG separately after PBT prepolymer was obtained (two-step strategy). The following described the detailed process for the synthesis of PBT-PTMG using these two different strategies (Scheme 1). In the one-step strategy, predetermined amount of PTA, BDO, PTMG and first portion of catalyst (titanium(IV) butoxide, 0.05 wt% of PTA) were added to a 1 L

autoclave. The mixture was placed under vacuum (0.1 kPa) and then purged with N_2 gas. This cycle was repeated for three times. Subsequently, the mixture was heated to 220 °C under N_2 until the amount of the distilled water reached 95% of its theoretic amount. Antioxidant 1010 (0.025 wt% of PTA) and second portion of catalyst (titanium(IV) butoxide, 0.05 wt% of PTA) were added and the system was sealed and evacuated below 20 Pa, and simultaneously heated up to 250 °C. This polycondensation reaction was conducted for a certain period time under mechanical stirring until the torque value reached a certain amount to ensure similar molecular weights of the products. The polymer was poured into cooling water and then dried at 50 °C under vacuum and kept still for further studies.



Scheme 1 Synthetic routes for preparation of PBT-PTMG copolymer using PTA as starting material: (a) one-step strategy and (b) two-step strategy

For the two-step strategy, the mixture of PTA, BDO and the catalyst was reacted under the same aforementioned conditions in order to get PBT pre-polymer in the first step. The system was then cooled to 180 °C, and antioxidant 1010, second portion of catalyst and PTMG were added. The system was sealed and evacuated to 1 kPa, and heated up to 230 °C and maintained for 1 h, after which, the system was placed under higher vacuum (below 20 Pa) and higher temperature (250 °C) for a certain period until the torque value reached a certain amount to ensure similar molecular weights for the products.

For both strategies, the ratio of BDO to PTA was kept at 1.5. The sample is denoted as PTMG wt%- M_n (PTMG)-S, where S (1 or 2) stands for the synthetic strategy. For example, 30-1000-1 means that the polymer contains 30 wt% of PTMG soft segment, PTMG with M_n of 1000 was used as the soft segment and the one-step strategy was used. All resulted polymers were used without further treatment.

Characterization

Molecular weights and molecular weight distributions were measured on a PL-GPC220 high temperature GPC. HPLC grade chloroform was used as elution solvent at 40 °C and molecular weight was calibrated with polystyrene standards. The concentration of all samples was 20 mg/3 mL. For samples with poor solubility in chloroform, a drop of 2-chlorophenol was used to dissolve the samples.

Intrinsic viscosity (IV) ($[\eta]$) was calculated from the elution time of the sample solution and the solvent measured in an AV370 Ubbelohde auto Ubbelohde viscometer equipped with a capillary tube with a diameter of 0.792 mm in a water bath at temperature of (25 ± 0.1) °C. The solvent used for the measurement was phenol-tetrachloroethane mixture (1/1, W/W), and the concentration of the sample was 0.125 g/25 mL. The following equation was used to calculate the IV^[24], where η_r is the relative viscosity:

$$[\eta] = \frac{\sqrt{1+1.4(\eta_r - 1)} - 1}{0.35}$$

Structure and compositions of PBT-PTMG were determined by proton nuclear magnetic resonance (¹H-NMR) in CDCl₃ solvent using a Bruker AVIII400 NMR spectrometer at room temperature. One drop of trifluoroacetic acid was added to the solution to dissolve the samples with poor solubility in CDCl₃.

Tensile testing was performed by using an Instron5567 tensile testing machine with a 500N load cell. The stretching rate was 100 mm/min and the test temperature was 25 °C. Dumb-bell-shaped sample bars with dimensions of 35.0 mm (length), 3.0 mm (neck width) and 0.5 mm (thickness) were prepared by press-molding at temperature 20 °C higher than T_m of the sample and subsequently cooled down to temperature below its T_c without releasing the pressure. All data were obtained by averaging the data from five parallel measurements.

Cyclic tensile testing was done with an Instron 5567 apparatus. The dumb-bell-shaped sample bars with dimensions of 35.0 mm (length), 3.0 mm (width), and 0.5 mm (thickness) were stretched to an ε_m of 200% elongation at room temperature with a 100 mm/min stretching rate. Then the clamps began to return with a speed of 50 mm/min until the force on the sample was zero. After the above two steps, one cycle was complete. Three samples were tested to calculate mean values and standard deviation. Every sample was subjected to 5 cycles and the shape recovery rate (R_r) was calculated according to the following equation:

$$R_r(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N-1)}$$

where N is the cycle number, ε_m is the maximum strain imposed on the material, $\varepsilon_p(N)$ and $\varepsilon_p(N-1)$ are the strains of the sample in two successive cycles when the force on the sample is 0 and $R_r(N)$ is based on two successive cycles.

DSC measurements were performed using a differential scanning calorimeter (Mettler-Toledo DSC 1). Measurements were performed under a nitrogen atmosphere at a flow rate of 50 mL/min. About 5 mg of sample was placed in an alumina sample pan and the measurement was carried out according to the following process: the sample was heated up to 260 °C at 10 K/min and held at this temperature for 4 min to erase the heat history. It was then cooled down to -40 °C at 10 K/min. Subsequently, a second heating scan was performed at 10 K/min to 260 °C. The melting point (T_m) and heat of fusion (ΔH_m) were obtained from the second heating scan and the crystallization temperature (T_c) was taken from the cooling scan. The degree of crystallinity was calculated according to the following equation:

$$\chi_c(\%) = \frac{\Delta H_m}{f \times \Delta H_m^0} \times 100\%$$

where χ_c is the percentage of crystallinity, f is the weight fraction, ΔH_m is the experimental melting heat of fusion, and ΔH_m^0 is the heat of fusion of 100% crystalline (140 J/g for PBT and 171.9 J/g for PTMG)^[16].

Thermal stability measurements were conducted using a TGA instrument (Mettler-Toledo TGA/DSC thermogravimetric analysis). For each sample, 6–10 mg sample was placed in a ceramic furnace and the TGA

curve was recorded ranging from 50 °C to 800 °C with a heating rate of 10 K/min under dry nitrogen atmosphere with a flow rate of 50 mL/min. We took the temperature at which the weight loss was 5% ($T_{5\%}$) as an index to evaluate the thermal stability of the sample.

RESULTS AND DISCUSSION

Synthesis and Composition of PBT-PTMG Copolymers

Two different strategies are used for the synthesis of a series of PBT-PTMG copolymers with different contents and molecular weights of PTMG using PTA as starting material. Table 1 shows the molecular weights and intrinsic viscosities of the PBT-PTMG products. For the PBT-PTMG with low PTMG content (30 wt%), both strategies are able to get high molecular weight products. For PBT-PTMG with high PTMG content (70 wt%), the one-step strategy fails to give high molecular weight products, M_n s are only 3000 and 4000 g/mol for 70-1000-1 and 70-2000-1, respectively. The two-step strategy successfully results in products with high molecular weights around 30000 g/mol for both 70-1000-2 and 70-2000-2. These results indicate that, by using different PTMG feeding strategies, the amount of PTMG has significant effect on the molecular weight of the final products, while the molecular weight of PTMG has no effect on the molecular weight of the products. This effect is due to the low activity of the terminal hydroxyl groups in PTMG during the esterification reaction with PTA in the one-step feeding strategy. Additionally, large amount of PTMG hinders the esterification reaction between PTA and BDO. Consequently, no high molecular weight product can be obtained with one-step feeding strategy when large amount of PTMG was used. On the other hand, for the two-step strategy, PTMG undergoes transesterification reaction with PBT prepolymer. This reaction is more favorable than esterification reaction between PTMG and PTA. As a result, high molecular weight products can be obtained even when large amount of PTMG was used. It is worth noting that small amount of PTMG does affect the esterification reaction in the one-step feeding strategy since it takes longer time to get 95% theoretical amount of water during the esterification step.

Table 1. Molecular weights, intrinsic viscosities and composition of PBT-PTMG copolymers

Samples	M_n^a (g/mol)	PDI ^a	$[\eta]^b$ (dL/g)	PTMG (wt%)		PTMG (mol%)		x^d		n^e	
				Feed	Final ^c	Feed	Final ^c	Feed	Final ^c	Feed	Final ^c
30-1000-1	23000	2.0	1.30	31.6	30.1	9.1	9.8	10.0	9.2	12.0	10.3
30-1000-2	27000	2.0	1.36	31.6	30.1	9.1	10.2	10.0	8.8	12.0	9.7
30-2000-1	26000	2.0	1.36	31.2	31.1	5.0	8.1	19.1	11.4	22.7	13.9
30-2000-2	28000	1.5	1.37	31.2	31.0	5.0	6.7	19.1	14.0	22.7	17.4
70-1000-1	3000	4.4	/	71.8	69.3	35.7	36.6	1.8	1.7	12.0	10.1
70-1000-2	29000	2.4	1.56	71.8	70.4	35.7	35.4	1.8	1.8	12.0	11.5
70-2000-1	4000	2.2	/	68.8	67.9	21.4	23.1	3.7	3.3	22.7	19.7
70-2000-2	32000	2.5	1.90	68.8	67.7	21.4	20.2	3.7	4.0	22.7	23.5

^a Determined by GPC; ^b Intrinsic viscosity; ^c Calculated from ¹H-NMR; ^d Average PBT hard segment length; ^e Number of PTMG repeating unit

Besides the effect on molecular weight of the PBT-PTMG copolymer, further investigation on the composition of the copolymer suggests additional different effects of these two strategies on the segment length of the PBT-PTMG copolymers. Figure 1 shows the ¹H-NMR spectra of PBT prepolymer, PTMG as well as PBT-PTMG copolymer. All peaks with different chemical shifts can be assigned accordingly to protons in the copolymer according to the literature^[25, 26]. We pay special attention to the peaks at $\delta = 4.44$ (b), 4.37 (b'), and 3.41 (e), which could be assigned to the protons in $-\text{OCH}_2-$ next to aromatic ring in hard segment, $-\text{OCH}_2-$ next to aromatic ring in soft segment and $-\text{OCH}_2-$ in PTMG repeating units, respectively. The compositions and segment lengths of the PBT-PTMG copolymers are then calculated based on the integration of these three peaks, A_b , $A_{b'}$, and A_e according to equations (1)–(4) and are listed in Table 1. In these equations, x is the average PBT hard segment length and n is the number of PTMG repeating unit ($-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$) incorporated into the copolymer, namely, the soft segment length.

$$x = \frac{A_b}{A_{b'}} \quad (1)$$

$$n = \frac{A_e}{A_{e'}} \quad (2)$$

$$\text{PTMG wt}\% = \frac{(72n+132)A_{b'}}{(72n+132)A_{b'} + 220A_b} \quad (3)$$

$$\text{PTMG mol}\% = \frac{1}{1+x} \quad (4)$$

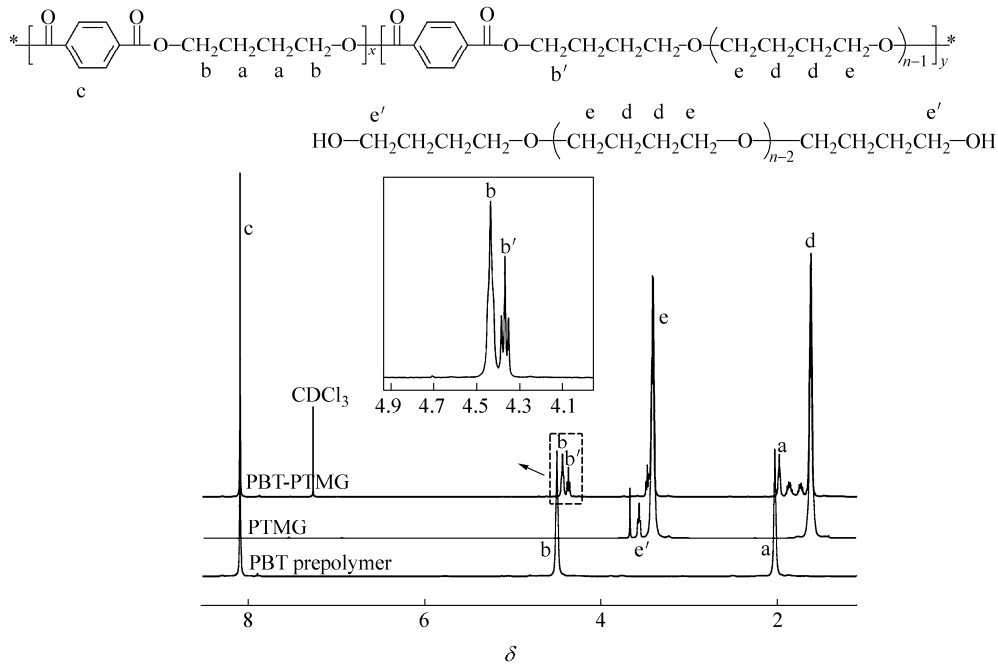


Fig. 1 ^1H -NMR spectra of PBT prepolymer, PTMG and PBT-PTMG copolymer

From Table 1, we observe that all resulted PBT-PTMG copolymers have final PTMG contents close to the feed ones, while final x and n are smaller than the feed ones, which mainly due to the degradation of PTMG soft segments. The degradation of PTMG not only decreases the number of repeating units in PTMG soft segments, but also results in decreasing of the average PBT hard segment length^[7]. Interestingly, with different PTMG contents and molecular weights, and especially with different feeding strategies, the profiles for the degradation of PTMG vary in a wide range. For the PBT-PTMG copolymers with PTMG M_n of 1000, the final x and n are slightly smaller than the feed ones. The degradation of PTMG during the synthesis results in depletion of only 0.5 to 2.3 repeating units in the PTMG chain. Additionally, with different PTMG contents and feeding strategies, there is no significant difference in x and n of the products, and the difference is merely around 5%. However, when PTMG with M_n of 2000 is used, the degradation of PTMG depends strongly on the PTMG contents and feeding strategies. Firstly, the degradation of PTMG is more serious for copolymers with low PTMG content than those with high PTMG content. It was reported in the literature that formation of long sequence of soft segments was more likely in PBT-PTMG with higher soft segment contents^[27]. For example, by using one-step strategy, almost ten repeating units in PTMG segments are degraded for sample 30-2000-1, while there are only three repeating units lost in PTMG segments for sample 70-2000-1. Secondly, the degradation of PTMG is of

smaller extent by using two-step strategy. There is a loss of less than five repeating units in the PTMG segments for sample 30-2000-2, comparing with a depletion of almost ten repeating units in the PTMG segments for sample 30-2000-1. These results reveal that two-step strategy not only results in high molecular weight products, regardless of PTMG content, but also decreases the degradation of PTMG segments. Therefore, the two-step strategy is better than the one-step strategy for the synthesis of PBT-PTMG copolymers with PTA, BDO and PTMG as starting materials.

Mechanical Properties

We first characterize the mechanical properties of PBT-PTMG copolymers by tensile testing and the results are summarized in Table 2. For the PBT-PTMG copolymers with high PTMG content, we do not include the mechanical properties of the two samples obtained from one-step strategy, namely 70-1000-1 and 70-2000-1, because their M_n s are too low to gain tensile strength. The other two samples (70-1000-2 and 70-2000-2) produced by two-step strategy have Young's modulus (E) of 18.3 and 12.2 MPa and tensile strength (σ_t) of 14.3 and 26.2 MPa and elongation at break (ε_b) of 1437.9% and 1643.1%, respectively. These mechanical properties are comparable with those of the ones obtained from traditional method with DMT, BDO and PTMG as starting materials using one-step strategy^[28]. When it comes to PBT-PTMG copolymers with low PTMG content, the results are different when PTMG M_n is different. In the first place, for the samples with PTMG M_n of 1000, both synthetic strategies result in products with similar E and σ_t . However, one-step strategy results in PBT-PTMG copolymer with much higher ε_b than that of two-step product, which are 1022.4% and 634.6% respectively. This can be attributed to the different segment lengths of the copolymers. 30-1000-1 has relatively longer soft segment length than that of 30-1000-2 (10.3 versus 9.7 as showed in Table 1). It has been reported in the literature that with longer soft segment, the ε_b will be higher^[29]. Secondly, for the samples with PTMG M_n of 2000, two-step product 30-2000-2 has much higher E but lower σ_t and ε_b than one-step product 30-2000-1. Higher E is because of longer average PBT hard segment^[9], while lower σ_t and ε_b is due to the strain-induced crystallization of longer soft segments^[29]. This strain-induced crystallization of PTMG occurs only when the content of PTMG as well as the segment length of PTMG reaches a certain value^[29, 30]. Obviously, there is a strain-induced crystallization of PTMG in sample 30-2000-2, which results in lower ε_b . As a result, only two-step strategy can successfully result in PBT-PTMG copolymers with good mechanical properties when PTMG content is high, while both strategies are suitable for the ones with low PTMG content. Furthermore, in the case of PBT-PTMG copolymers with low PTMG content, two-step strategy sacrifices the ε_b while one-step strategy seems to compromise E and ε_b .

Table 2. Mechanical properties of PBT-PTMG copolymers

Samples	E (MPa)	σ_t (MPa)	ε_b (%)	σ_y (MPa)	ε_y (%)
30-1000-1	157.5 ± 6.6	39.3 ± 2.7	1022.4 ± 21.8	23.2 ± 0.8	30.6 ± 1.0
30-1000-2	170.9 ± 8.0	27.5 ± 2.3	634.6 ± 36.0	23.3 ± 1.2	28.0 ± 0.9
30-2000-1	165.8 ± 11.9	38.7 ± 1.1	932.1 ± 18.6	20.4 ± 1.2	27.7 ± 0.7
30-2000-2	253.5 ± 2.7	27.2 ± 1.5	547.5 ± 38.6	22.2 ± 0.5	20.0 ± 2.0
70-1000-2	18.3 ± 0.3	14.3 ± 0.2	1437.9 ± 13.5	5.9 ± 0.1	57.2 ± 0.5
70-2000-2	12.2 ± 1.0	26.2 ± 1.1	1643.1 ± 45.1	6.5 ± 0.2	81.4 ± 2.4

Shape Recovery

In order to evaluate the effect of feeding strategy on the shape recovery property of PBT-PTMG copolymer, we also perform the cyclic tensile testing for PBT-PTMG copolymers with 30 wt% of soft segment. The recovery rates of the cyclic tensile testing with 200% strain are showed in Table 3. For the copolymers with PTMG M_n of 1000, it can be found that one-step product has relatively higher recovery rate compared with two-step one in the first cycle, which are 23.6% for 30-1000-1 and 19.8% for 30-1000-2, respectively. This is probably due to the different soft segment lengths in the copolymers. 30-1000-1 has a soft segment length of 10.3, which is relatively higher than that of 30-1000-2, which is 9.7. It was reported in the literature that with longer or richer soft segment, the copolymer tended to have higher recovery rate^[16]. On the other hand, the copolymers with PTMG

M_n of 2000 are different. 30-2000-1 has a soft segment length of 13.9 with recovery rate of 19.6%, while 30-2000-2 has a soft segment length of 17.4 with recovery rate of only 16.5%. These results indicate that for the copolymers with PTMG M_n of 2000, although the one-step product has relatively shorter soft segment length than that of the two-step one, it has higher recovery rate. This observation on shape recovery property is similar to the results of elongation at break. The decrease of recovery rate is probably also due to the strain-induced crystallization of PTMG soft segment. The PTMG chains in amorphous phase would orient along the stretching direction and form PTMG crystals, and this transition of amorphous phase to crystal phase is irreversible. When the stress exceeds the interaction limit among the lately formed PTMG crystal, the PTMG chains will slip, which will result in unrecoverable deformation. Therefore, with longer soft segment length, the strain-induced crystallization of PTMG occurs at lower strain^[30], resulting in lower recovery rate.

Table 3. The recovery rate at 200% strain of the cyclic tensile testing

Samples	R_r (1)%	R_r (2)%	R_r (3)%	R_r (4)%	R_r (5)%
30-1000-1	23.6 ± 0.3	95.3 ± 0.5	97.6 ± 0.7	97.8 ± 0.2	98.4 ± 0.4
30-1000-2	19.8 ± 0.9	97.5 ± 0.8	98.4 ± 0.7	98.9 ± 1.0	99.2 ± 1.1
30-2000-1	19.6 ± 0.1	95.0 ± 0.7	97.4 ± 0.9	98.3 ± 0.8	98.9 ± 0.9
30-2000-2	16.5 ± 0.9	94.1 ± 1.6	96.7 ± 1.0	97.6 ± 0.8	98.3 ± 0.9

Thermal Analysis

The melting behavior, crystallization of PBT-PTMG copolymers are compared and summarized in Table 4. The melting temperatures of the samples are obtained from second heating scans and the crystallization temperatures are collected from the cooling scans, as showed in Figs. 2(a) and 2(b) respectively. The melting behavior and crystallization of PBT-PTMG copolymers are quite different with respect to feeding strategy of PTMG when content and molecular weight of PTMG are constant. On the one hand, PBT-PTMG copolymers series with 30% of soft segment have similar thermal properties regardless of PTMG feeding strategy. For example, both 30-1000-1 and 30-1000-2 samples have $T_{m,h}$ of 208 °C, $T_{c,h}$ around 165 °C and $\chi_{c,h}$ around 32%. While for PBT-PTMG copolymers with higher PTMG molecular weight both 30-2000-1 and 30-2000-2 samples showed double melting and crystallization temperatures, which are from crystalline regions of soft and hard segments respectively. The $T_{m,h}$ and $T_{c,s}$ are around 215 °C and −18 °C for both samples, while $T_{m,s}$ and $T_{c,h}$ show slight difference. For 30-2000-1, both $T_{m,s}$ and $T_{c,h}$ are lower than those of 30-2000-2. This is because the sample from one-step strategy has relatively shorter hard and soft segment length than the one from two-step strategy. Furthermore, shorter hard and soft segment lengths also result in decreasing of crystallinity^[12]. On the other hand, PBT-PTMG copolymers with 70% of soft segment showed significantly different thermal properties with respect to PTMG feeding strategy. PBT-PTMG samples obtained from one-step strategy have lower $T_{m,h}$ but higher $T_{c,h}$ in comparison with the ones obtained by two-step strategy. For example, $T_{m,h}$ is 10 K lower but $T_{c,h}$ is 20 K higher for sample 70-1000-1 compared with 70-1000-2. This obvious difference in thermal properties is due to the large difference of the M_n of the PBT-PTMG copolymers. Interestingly, although 70-2000-1 has

Table 4. Thermal properties of PBT-PTMG copolymers

Samples	$T_{m,s}$ (°C)	$T_{m,h}$ (°C)	$\Delta H_{m,s}$ (J/g)	$\Delta H_{m,h}$ (J/g)	$T_{c,s}$ (°C)	$T_{c,h}$ (°C)	$\chi_{c,s}$ (%)	$\chi_{c,h}$ (%)	$T_{5\%}$ (°C)
30-1000-1	/	208	/	31	/	167	/	31.7	364
30-1000-2	/	208	/	32	/	164	/	32.7	363
30-2000-1	10	215	6	21	−18	170	11.2	21.8	364
30-2000-2	21	216	9	26	−18	176	16.9	26.9	367
70-1000-1	/	145	/	14	/	111	/	32.6	339
70-1000-2	/	153	/	11	/	91	/	26.5	291
70-2000-1	10	178	22	12	−30	141	18.8	26.7	348
70-2000-2	5	183	13	15	−27	114	11.2	33.2	334

$T_{m,s}$ and $T_{m,h}$ are melting temperatures of soft and hard segments respectively; $\Delta H_{m,s}$ and $\Delta H_{m,h}$ are heat of fusion of soft and hard segments respectively; $T_{c,s}$ and $T_{c,h}$ are crystallization temperature of soft and hard segments respectively, and $\chi_{c,s}$ and $\chi_{c,h}$ are degree of crystallinity of soft and hard segments respectively.

shorter soft segment length than 70-2000-2, it shows higher $T_{m,s}$. This is because 70-2000-1 has also lower molecular weight and shorter hard segment length than 70-2000-2, which results in less influence on the crystalline region of soft segment domain, thus 70-2000-1 has higher $T_{m,s}$ as well as higher $\chi_{c,s}$. Therefore, when PTMG content is low, both strategies are suitable for the synthesis of PBT-PTMG copolymer with good thermal properties. However, when high PTMG content is required, two-step strategy is better than one-step one in order to get PBT-PTMG copolymer with high molecular weight and good thermal properties.

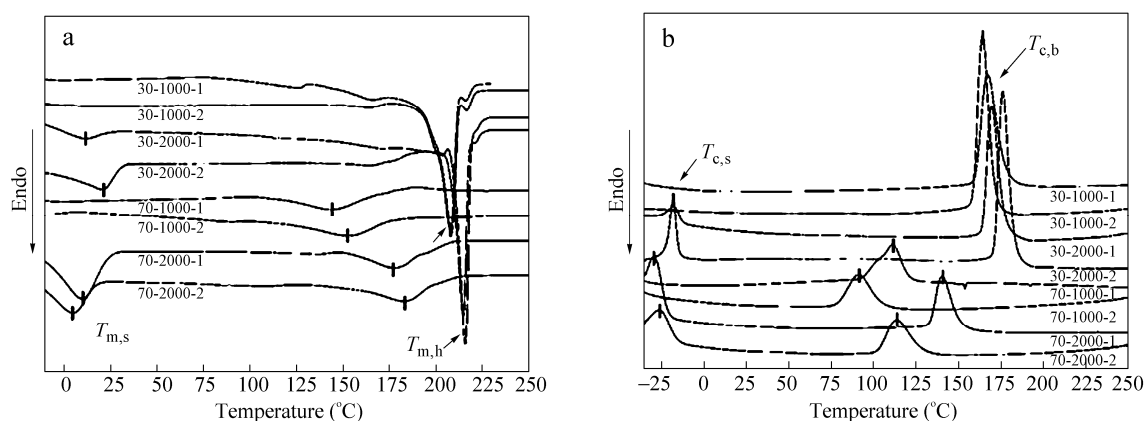


Fig. 2 DSC curves for PBT-PTMG copolymers: (a) second heating scans and (b) cooling scans

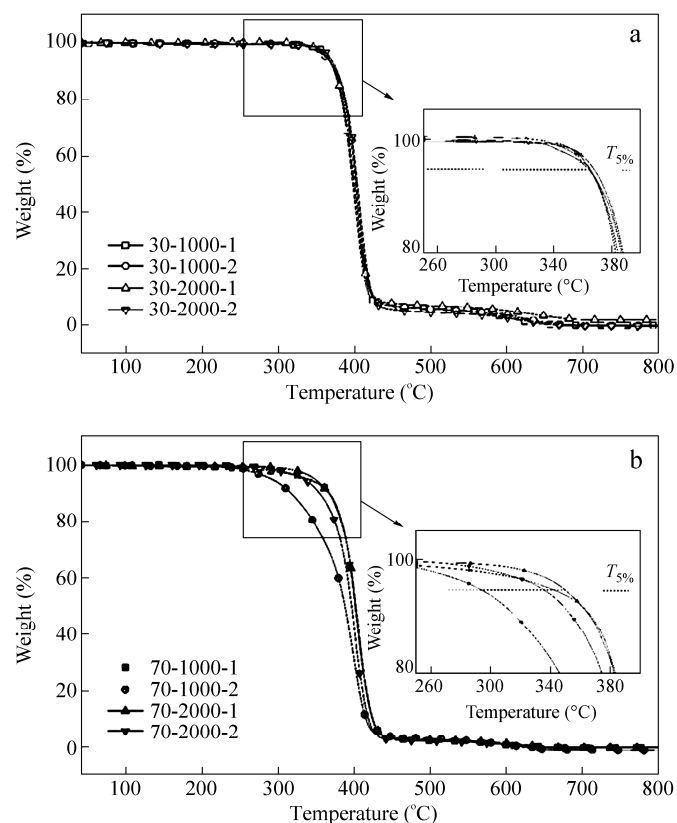


Fig. 3 TGA curves for PBT-PTMG copolymers: (a) 30 series and (b) 70 series

The thermal stability of the PBT-PTMG copolymers is characterized by TGA as showed in Fig. 3 and the results are showed in Table 4. All samples with 30% soft segment have similar thermal stability with $T_{5\%}$ around 365 °C regardless of PTMG feeding strategy. While samples with 70% soft segment that resulted from two-step strategy have lower thermal stability compared with those from one-step strategy. These results can be ascribed to the decrease of thermal stability of PTMG soft segment with the increase of its segment length and content in the copolymer. In addition, although 70-2000-2 has longer soft segment length than 70-1000-2, it has much higher $T_{5\%}$ than 70-1000-2. This is due to longer hard segment length in 70-2000-2 than in 70-1000-2.

CONCLUSIONS

A series of PBT-PTMG copolymers with different PTMG contents and molecular weights are synthesized with one-step and two-step melt polycondensation using PTA, BDO and PTMG as starting materials. With low soft segment content, both one-step and two-step strategies are suitable for the synthesis of PBT-PTMG copolymers with high molecular weight and similar thermal properties, while the mechanical properties are slight different. One-step strategy product has relatively lower modulus and tensile strength, but higher elongation at break and shape recovery rate, in comparison with those of two-step strategy product. On the other hand, when the soft segment content is high, the one-step strategy fails to give high molecular weight products, only two-step strategy successfully results in PBT-PTMG copolymers with comparable molecular weight as well as thermal and mechanical properties similar to those from one-step strategy using DMT route. Furthermore, the two-step strategy tends to give PBT-PTMG copolymers with both longer hard and soft segments. Therefore, the two-step strategy is a better method than the one-step one when PTA is used in the synthesis of TPEEs with soft segment content ranging from low to high level. It effectively avoids the influence of polyether on the esterification of PTA with diol by simply feeding the polyether separately in the second step. This study suggests us a more effective two-step strategy for the synthesis of different TPEEs using PTA, instead of DMT, as starting material.

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