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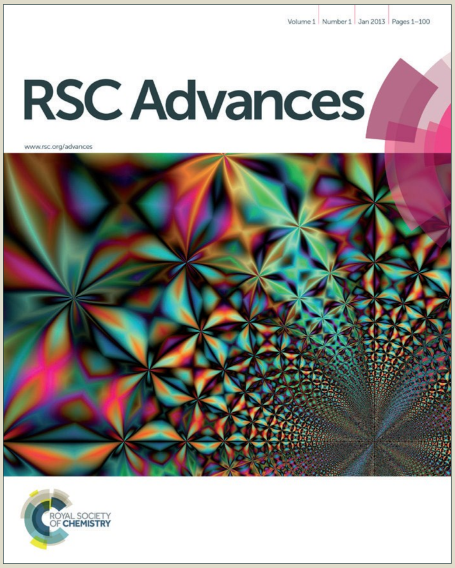

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Incorporation of 1,4-cyclohexanedicarboxylic acid into poly(butylene terephthalate)-*b*-poly(tetramethylene glycol) to Alter Thermal Properties without Compromising Tensile and Elastic Properties

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Thermal and tensile properties of thermoplastic elastomer (*e.g.* poly(butylene terephthalate)-b-poly(tetramethylene glycol) (PBT-PTMG)) are usually tuned by changing the composition of hard and soft segment parts.Simply increasing the amount of soft segment results in lower melting temperature and better elastic properties, but the thermal stability and tensile properties are inevitably sacrificed. In this work, by incorporation of an aliphatic ring structure (*i.e.* 1,4-cyclohexanedicarboxylic acid) (CHDA) to partially replace aromatic ring (*i.e.* terephthalic acid) in PBT-PTMG, the properties of the material can be tuned in such a way that the melting temperature decreases, while the thermal stability, tensile and elastic property are not compromised. Moreover, manipulation over the stereo–chemistry of CHDA unit discloses the "elastic" nature of the non-planar ring structure. Samples with more amount of *cis*-CHDA tend to have better tensile and elastic properties compared with their *trans*-CHDA counterparts.

Introduction

Thermoplastic elastomers (TPEs) are highly valuable materials and have been used widely for many years. Typically, TPEs are consisted with two parts, *i.e.* hard segment and soft segment. The hard segment is either crystalline polymer with high melting temperature (T_m) (*e.g.* poly(butylenes terephthalate) (PBT)),[1–3] glassy polymer with high glass transition temperature (T_g) (*e.g.* polystyrene (PS)),[4] or amorphous polymer with strong interactions such as hydrogen bonding (*e.g.* polyurethane (PU)).[5–7] While the soft segment is amorphous polymer with low T_g (*e.g.* polyolefin or polyether).[8–13] These two segments form a well studied micro-phase separation structure.[14–17] The hard segment is responsible for the processibility of TPEs like plastic under high temperature, and the soft segment endows TPEs with elasticity resembling rubber at room temperature.[8]

Generally, materials with high T_m and low thermal stability (typically represents by $T_{5\%}$, temperature at which the weight loss of the material is 5%) are inevitable to initiate poor processibility. Thus it is necessary to simultaneously decrease the T_m and increase the thermal stability to gain excellent processibility. Usually, the processibility as well as the tensile properties of TPEs can be facilely tuned by changing the composition of the hard and soft segments.[14,18–20] For example, in the case of thermoplastic poly(ether-ester) elastomers (TPEEs), increasing amount of soft segment gives lower T_m and better elasticity.[5,12] However, it also comes with decrease of thermal stability as well as tensile modulus and strength, resulting from poor thermal stability and tensile properties in the present of large amount of soft segment.[4,8] As a result, neither processibility nor tensile properties of the material can be enhanced by simply adjusting the composition. Other than adding more amount of soft segment, an alternative strategy is therefore strongly required. Incorporation of a third monomer is an interesting method to obtain better processibility without compromising tensile properties. According to this strategy, the most important concern is the type of the third monomer. Previously, succinic acid[21] was used to form a modified TPEE, poly[(butylene succincate)-*co*-(butylene terephthalate)]-*b*-poly(ethylene glycol).[22,23] When the amount of poly(butylene succinate) (PBS) was 20%, although the T_m decreased for almost 35°C and the thermal stability remained relatively unchanged, the tensile modulus and strength decreased for 42 and 32%, respectively.[23] Therefore, a third monomer other than succinic acid is desired.

Monomers with aliphatic ring structure, such as 1,4-cyclohexanedicarboxylic acid (CHDA), have similar rigidity to their aromatic counterparts but show even better thermal stability when incorporated to the polymer chain.[24–27] Incorporation of CHDA to PBT-PEG results in poly[(butylene

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1,4-cyclohexanedicarboxylate)-*co*-(butylene terephthalate)]-*b*-PEG (PBCT-PEG).[28] As expected, with the increasing amount of CHDA, the products have decreased T_m, but still decreased tensile modulus and strength. It is worth noting that the CHDA unit in this polymer has a *cis*/*trans* ratio of 65/35. According to our previous findings, polyester with large amount of *cis*-CHDA is amorphous and shows elastic behavior, while the one with large amount of *trans*-CHDA is semicrystalline and shows high tensile modulus and strength.[29] Thus the influence of stereochemistry on the properties of CHDA substituted TPEE is of great interesting. By altering the *cis*/*trans* ratio of CHDA, it is possible to fabricate novel TPEE with lower T_m but higher $T_{5\%}$ to induce improved processibility without reducing its tensile and elastic properties. In this work, we will use CHDA to replace or partially replace aromatic ring in the molecular structure of an important TPEE, namely, poly(butylene terephthalate)-*b*-poly(tetramethylene glycol) (PBT-PTMG).[8] The impact of the CHDA amount and its stereochemistry (*i.e.* *cis*/*trans* ratio) on the properties, including T_m, $T_{5\%}$, tensile and elastic properties, of the resulted poly[(butylene 1,4-cyclohexanedicarboxylate)-*co*-(butylene terephthalate)]-*b*-PTMG (PBCT-PTMG) copolymers will be fully investigated.

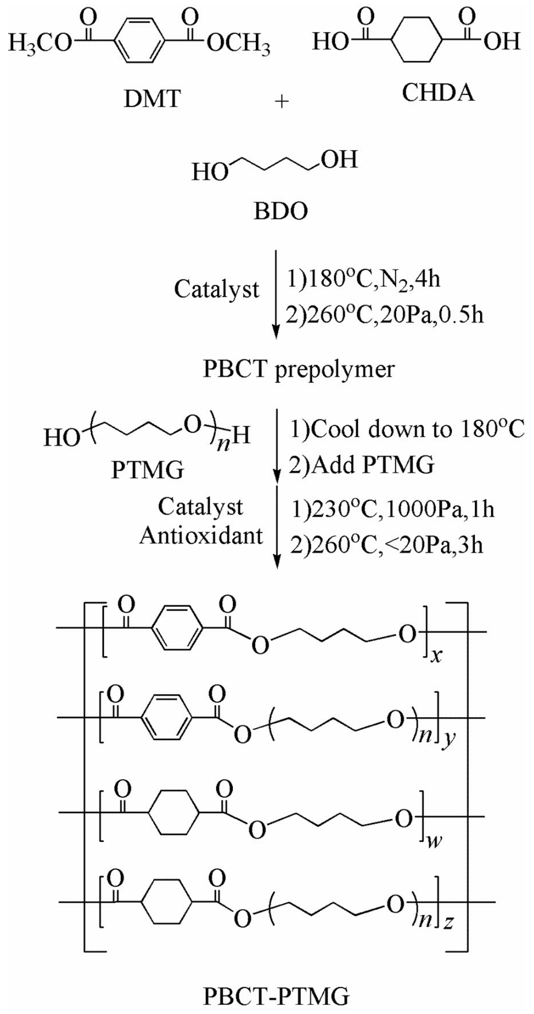
Materials and methods

Materials

Dimethylene terephthalate (DMT), 1,4-butanediol (BDO), PTMG with M_n of 1000 g/mol, titanium(IV) butoxide and antioxidant1010 were all purchased from Aladdin Reagent Co. Ltd (Shanghai, China). Chloroform was obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). *trans*-1,4-cyclohexanedicarboxylic acid (*trans*-CHDA) (99%) and *mix*-1,4-cyclohexanedicarboxylic acid (*mix*-CHDA) with a *cis*/*trans* ratio of 50/50 were purchased from Nanjing Chemlin Chemical Industry Co., Ltd. *cis*-CHDA (97%) was obtained by separation and purification of *mix*-CHDA from ethanol according to methods described in the literatures.[30,31] All the chemicals are used as received without further treatment.

Synthesis of PBCT-PTMG copolymer

We prepared the PBCT-PTMG copolymers by melt polycondensation technique with DMT as starting material. More importantly, PTMG was feed separately after PBCT prepolymer was obtained.[8] The following described the detailed process for the synthesis of PBCT-PTMG copolymer (Scheme 1). In a typical reaction for the synthesis of 30-10-90 as showed in Table 1, DMT (191.0g), CHDA (21.2g), BDO (247.5g) and first portion of catalyst (titanium(IV) butoxide, 0.05*wt*% of DMT, 0.0955g) were added to a 1L autoclave. The mixture was placed under vacuum (0.1kPa) and then purged with N_2 gas. This cycle was repeated for three times. Subsequently, the mixture was heated to 180° C under N_2 until the amount of the distilled water reached 95% of its theoretic amount (typically 4h). The system was then evacuated below 20Pa, and simultaneously heated up to 230 ° C. This pre-polycondensation process was conducted for about 0.5h to allow the formation of PBT/PBC prepolymer. The system was then cooled to 180° C, and antioxidant 1010 (0.53g), second portion of catalyst (0.0955g) and PTMG (82.0g) were added.



Scheme 1 Synthesis of PBCT-PTMG thermoplastic elastomer.

Subsequently, the system was sealed and evacuated to 1kPa, and heated up to 230° C and maintained for 1h, after which, the system was subject to higher vacuum (below 20Pa) and higher temperature (260° C) for about 3-5h to ensure similar molecular weights for the products.

The ratio of diol to dicarboxylic acid was kept at 2.5. Samples without CHDA were also prepared via the same synthetic route. All samples were denoted as PTMG *wt*%-CHDA *mol*%-*trans*-CHDA *mol*%. For example, 30-10-50 means that the polymer contains 30*wt*% of PTMG soft segment, 10*mol*% CHDA (*i.e.* 90*mol*% DMT) and the ratio of *trans* isomer of CHDA is 50*mol*%. All resulted polymers were used without further treatment.

Instruments and characterization methods

Molecular weights and molecular weight distributions were measured on PL-GPC220 high temperature gel permeation chromatography (GPC). Structure and compositions of PBCT-

PTMG copolymers were determined by proton nuclear magnetic resonance (1H NMR) in $CDCl_3$ solvent using a Bruker AVIII400 NMR spectrometer at room temperature. Differential scanning calorimetry (DSC) measurements were performed using a differential scanning calorimeter of type METTLER-TOLEDO DSC I. Thermal stability measurements were conducted using a Mettler-Toledo TGA/DSC thermogravimetric analysis (TGA). Tensile testing and cyclic tensile testing were performed in an Instron5567 tensile testing machine with a load cell of 500 N.

Detailed information about the characterization is provided in Electronic Supplementary Information (ESI).

Results and discussion

Structure and composition of PBCT-PTMG copolymer

PBCT-PTMG copolymers varying in CHDA amount and *cis*/*trans* ratio are successfully synthesized via a modified two-step strategy[8] using DMT route (Scheme 1). DMT other than terephthalic acid (PTA) is used because of the concerning on the isomerization control over CHDA. The isomerization reaction of CHDA between *cis* and *trans* isomers takes place under high temperature[28] and would reach a thermodynamically balanced ratio of 34/66.[32] An important purpose of current work is to study the influence of stereochemistry of CHDA on the properties of PBCT-PTMG copolymer, thus the control over *cis*/*trans* ratio is crucial. The final *cis*/*trans* ratio would be close to the feed one if the isomerization reaction is suppressed. And the most effective and simplest way to achieve this goal is to reduce the reaction temperature.[28] Comparing with PTA route in which the esterification reaction occurs under higher temperature, the DMT route involves transesterification requiring relatively lower temperature.

Firstly, three PBT-PTMG copolymers vary in soft segment contents (sample 30-0-0, 40-0-0 and 60-0-0) are obtained without adding CHDA in order to compare the modification effect of CHDA. Secondly, three PBCT-PTMG copolymers with different substitution amount of CHDA over aromatic ring (sample 30-10-90, 30-20-90 and 30-100-90) are prepared. The ratio of *trans*-CHDA in these samples is kept at 90*mol*%. These series of PBCT-PTMG copolymers are used to investigate the influence of CHDA amount on the properties of the elastomers. And finally, maintaining the substitution amount of CHDA at 10*mol*%, another two PBCT-PTMG copolymers with lower ratio of *trans*-CHDA (sample 30-10-30 and 30-10-50) are synthesized to study the effect of stereochemistry of CHDA on the properties of PBCT-PTMG copolymers. *trans*-CHDA (99%), *mix*-CHDA (50/50) and *cis*-CHDA (97%) are respectively used as raw materials for the synthesis of PBCT-CHDA copolymers whose percentages of *trans*-CHDA are 90, 50 and 30*mol*%.

Figure 1 shows the ^1H NMR spectra of three typical PBCT-PTMG samples, namely 30-0-0, 30-10-50 and 30-100-90. All peaks with different chemical shifts can be attributed to correspondent protons in the products.[8,28,29] Particular attention is paid to the peaks located at δ = 4.44 (a), 4.37 (b), 4.15 (c), 4.08 (d) and 3.41 (b’ and d’), which could be assigned to the protons in $-OCH_2-$ next to aromatic ring in PBT hard segment, $-OCH_2-$ next to aromatic ring in PBT soft segment, $-OCH_2-$ next to CHDA in PBC hard segment, $-OCH_2-$ next to CHDA in PBC soft segment and $-OCH_2-$ in PTMG repeating units, respectively. Therefore, the composition of the PBCT-PTMG copolymers are calculated based on the integration of these five peaks, I_a, I_b, I_c, I_d and $I_{b'+d'}$ according to equations (S1)-(S5)(See ESI). Furthermore, peaks with chemical shifts at δ = 2.47 (e-*cis*) and 2.27 (e-*trans*) are signals from -CH- in *cis*- and *trans*-CHDA unit respectively, and the integration of these two peaks $I_{e\text{-}cis}$ and $I_{e\text{-}trans}$ can be used to calculate the ratio of *trans*-CHDA according to equation (S6)(See ESI). These results are summarized and collected in Table 1.

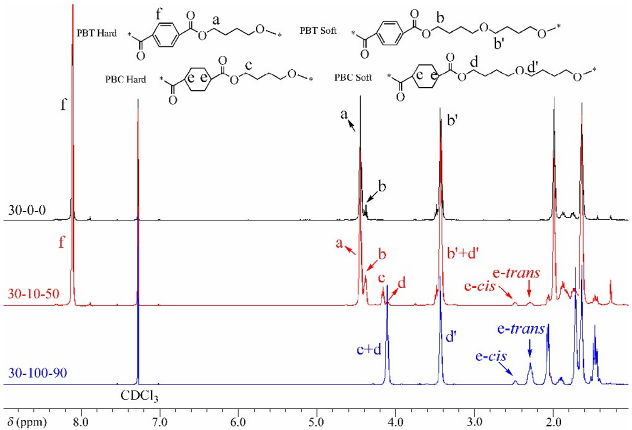


Figure 1 ^1H NMR (300MHz, $CDCl_3$) spectra of typical PBCT-PTMG samples.

All samples have comparable high molecular weights (M_n) and the molecular weight distributions (M_w/M_n) are in the range of 2.0 to 3.9. The compositions (including the amount of PBT and PBC hard segment as well as PBT and PBC soft segment) in the final products are in good agreement with the designed ones. More importantly, PBCT-PTMG copolymers with different CHDA substitution amount of 12.0, 23.7 and 100*mol*% are obtained, and the *trans*-CHDA contents in these three samples range from 87 to 92*mol*%. In addition, with CHDA substitution ratio of about 12.4 and 12.5*mol*%, samples containing 30 and 55*mol*% *trans*-CHDA are successfully obtained. The isomerization between *cis* and *trans* isomers of CHDA is effectively suppressed with only 7-12% and 5% deviation from the feed ones for samples with *trans*-CHDA (99%) and *mix*-CHDA (50/50) as starting materials respectively. While a 27% deviation is observed for sample with *cis*-CHDA (97%) as raw material because of large deviation from the thermodynamically balanced ratio (*cis*/*trans*=34/66).[29]

Thermal analysis

The thermal transition and stability of PBCT-PTMG copolymers are investigated by DSC and TGA measurements. Figure 2 shows the DSC curves of the first two series of PBCT-PTMG copolymers, the one with different amount of soft segment without CHDA and the one with different CHDA substitution amount. Relevant data are summarized in Table 2.

Firstly, the curves clearly show that with the increase of soft segment from 30 to 60*wt*%, the melting temperature T_m and crystallization temperature T_c of the hard segment decrease gradually from 208 to 173°C and from 164 to 120°C respectively, as expected. The degree of crystallinity of the hard segment χ_c also decreases a little bit. Secondly, incorporation of CHDA to replace aromatic ring results in a similar trend. The second series samples have decreased T_m, T_c as well as χ_c when larger amount of CHDA is introduced to substitute the aromatic ring. For example, the T_m of PBCT-PTMG decreases for 10, 25 and 70 °C with 10, 20 and 100*mol*% substitution respectively, while their χ_c are 30.8, 26.1 and 18.2% accordingly. This is because PBC with 90*mol*% of trans-CHDA has T_m and χ_c of 147°C and 19.4%,[29] showing lower crystallization ability comparing with PBT. Thus the presence of PBC (containing 90*mol*% of *trans*-CHDA) in the hard segment strongly reduces the crystallization ability of PBT hard segment, shifting T_m towards lower temperature.

Table 1 Compositions and molecular weights of PBCT-PTMG samples.[a]

Samples	PBT Hard Segment (*wt*%)	PBT Soft Segment (*wt*%)	PBC Hard segment (*wt*%)	PBC Soft segment (*wt*%)	CHDA (*mol*%)	*trans*-CHDA (*mol*%)	M_n ($\times10^4$)	M_w/M_n
30-0-0	69.9	30.1	0.0	0.0	0.0	0	2.7	2.0
40-0-0	60.3	39.7	0.0	0.0	0.0	0	2.8	2.6
60-0-0	41.2	58.8	0.0	0.0	0.0	0	1.9	2.8
30-10-90	56.3	31.2	7.5	5.0	12.0	89	1.5	3.9
30-20-90	44.1	31.8	14.1	10.0	23.7	92	2.3	3.5
30-100-90	0	0	/	/	100.0	87	3.5	2.5
30-10-30	55.3	32.0	8.0	4.8	12.4	30	2.5	3.3
30-10-50	55.9	31.1	8.1	4.8	12.5	55	2.4	3.0

a) The compositions are calculated from 1H NMR and molecular weight (M_n) and molecular weight distribution (M_w/M_n) are determined by GPC in $CHCl_3$.

More importantly, when it comes to the impact of stereochemistry of CHDA on the thermal transitions of PBCT-PTMG copolymers, Figure 3 reveals interesting trend. Decreasing the ratio of *trans*-CHDA, namely increasing the ratio of *cis*-CHDA, PBCT-PTMG copolymers have decreased T_m, T_c as well as χ_c. This trend is in consistent with that in PBC polyester reported in our recent work.[29] It has been predicted and showed experimentally that the structure of *trans*-CHDA is regular, while that of *cis*-CHDA is irregular.[25,33,34] Thus more amount of *trans*-CHDA tends to form stable crystal, resulting in relatively higher T_m, while *cis*-CHDA introduces “*kinks*” to the molecular chain and disrupts the formation of crystal. Therefore, for the calculation of χ_c of the hard segment, only the contribution from PBT and PBC with *trans*-CHDA is considered.

TGA analysis provides information about the thermal stability of PBCT-PTMG copolymers as showed in Figure 4. Not surprisingly, increasing the amount of soft segment from 30% to 60*wt*% results in not only smaller T_m, but also significantly lower thermal stability, due to the nature of PTMG soft segment. The $T_{5\%}$ of these samples decreases from 295 all the way down to 230°C. On the contrary, when CHDA takes the place of aromatic ring, it reduces the T_m, but improves the thermal stability. The $T_{5\%}$ of samples containing CHDA moiety are substantially higher than their counterparts without the aliphatic ring structure. Apparently, the aliphatic ring is less vulnerable to thermal decomposition than the aromatic ring, as indicated by many researchers.[24,25,35] The highest $T_{5\%}$ reaches 337°C for sample 30-20-90. Moreover, it seems that varying the stereochemistry of CHDA has little effect on the thermal stability of the samples.

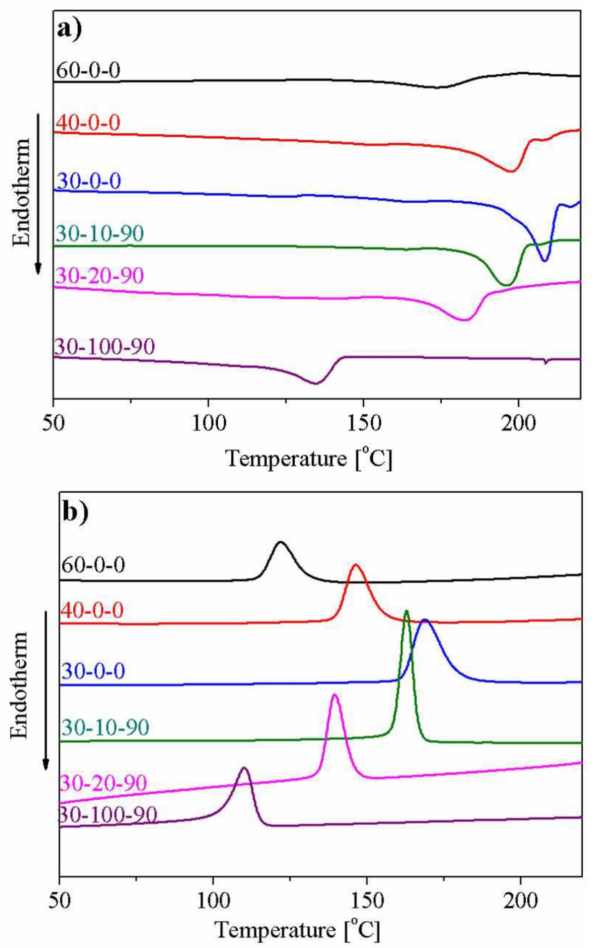


Figure 2 DSC curves for PBCT-PTMG samples with different amount of soft segment and CHDA: a) second heating and b) cooling scans.

Table 2 Thermal properties of PBCT-PTMG samples.[a]

Samples	T_m (°C)	ΔH_m (J/g)	T_c (°C)	χ_c (%)	$T_{5\%}$(Air) (°C)
30-0-0	208	31.6	164	32.3	295
40-0-0	196	22.5	146	26.6	264
60-0-0	173	15.5	120	26.8	230
30-10-90	196	24.6	163	30.8	306
30-20-90	183	17.0	140	26.1	337
30-100-90	134	15.6	110	18.2	309
30-10-30	188	18.9	139	26.9	307
30-10-50	193	22.5	156	30.1	317

a) melting temperature T_m, melting enthalpy ΔH_m and degree of crystallinity of hard segment χ_c are determined from second heating scan of DSC curve and the crystallization temperature T_c is determined from the cooling scan of DSC curve, the temperature at 5% weight loss is determined by TGA in air atmosphere.

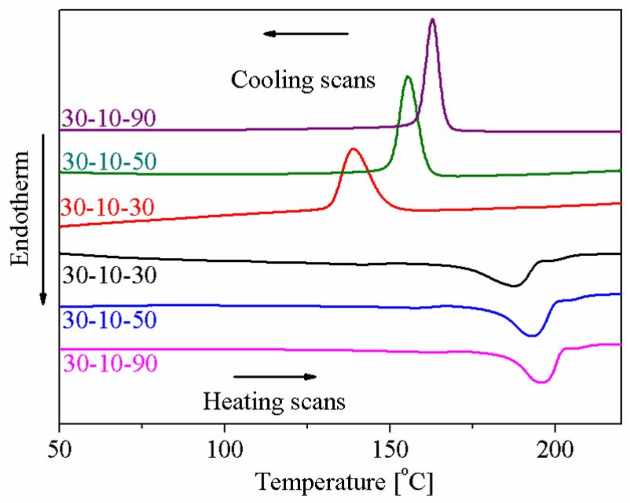


Figure 3 DSC curves for PBCT-PTMG samples containing 10*mol*% CHDA with different amount of *trans*-CHDA.

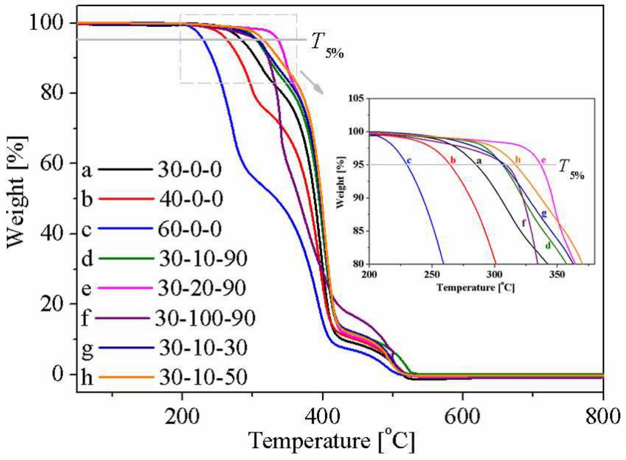


Figure 4 TGA curves for PBCT-PTMG samples

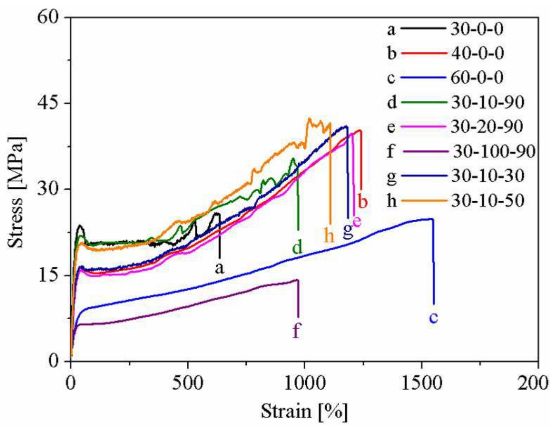


Figure 5 Representative tensile strain-stress curves of PBCT-PTMG samples

Table 3 Tensile properties of PBCT-PTMG samples.[a]

Sample	E (Mpa)	σ_t (Mpa)	ε_b (%)	σ_y (Mpa)	ε_y (%)

30-0-0	171±8	28±2	635±36	23.0±1.0	28±1
40-0-0	85±3	41±2	1223±50	15.0±0.2	36±1
60-0-0	29±2	24±1	1566±53	8.0±0.4	50±5
30-10-90	144±7	37±2	986±23	22.0±0.6	30±1
30-20-90	134±22	41±2	1230±31	16.0±0.3	31±6
30-100-90	39±2	14±1	960±24	6.0±0.1	29±1
30-10-30	142±17	41±2	1180±33	17.0±1.0	33±6
30-10-50	160±16	42±1	1109±22	20.0±1.0	33±5

a) Tensile modulus E, tensile strength σ_t, elongation at break ε_b, yield stress σ_y and yield strain ε_y are determined by tensile testing.

Tensile properties

Evidently, results from thermal analysis strongly imply that the processibility of PBCT-PTMG copolymers modified by addition of CHDA is significantly enhanced. Subsequently, tensile testing performed with PBCT-PTMG copolymers would reflect impact of CHDA to their tensile properties.

Figure 5 shows the representative strain-stress curves of all samples and the tensile properties are summarized in Table 3. In the first place, although increasing the soft segment amount from 30 to 60*wt*% gives an improvement on the elongation at break for 1.5 times from 635 to 1566%, it enormously sacrifices the tensile modulus, which is cut down for 83% from 171 to 29MPa. However, for these samples, the tensile strength does not alter a lot due to the strain-hardening effect.[36] In contrast, incorporation of small amount of CHDA (e.g. 10 or 20*mol*%) has different impact on tensile properties. Take sample 30-20-90 as an example, It not only enhances the tensile modules for 46% from 28 to 41MPa compared with 30-0-0, but also increases the elongation at break for 94% from 635 to 1230%. What's more important, this modification does not compromise too much tensile modulus, which only decreases for 22% from 171 to 134MPa. Interestingly, Wang et.al.[28] reported a PBT-PEG system with 10 to 40% amount of CHDA substitution over PTA. The CHDA had a final *cis*/*trans* ratio of 65/35. When the amount of CHDA increased from 10 to 20%, the tensile modulus decreased dramatically for 91.4%. In our case, there is only 7% loss in tensile modulus (sample 30-10-90 *vs.* 30-20-90) due to the fact that these two samples have CHDA with final *cis*/*trans* ratio of 10/90. Apparently, besides the CHDA substitution amount over DMT, the *cis*/*trans* ratio is also crucial for maintaining high tensile modulus. With higher ratio of *trans* isomer, the resulted material tends to have higher modulus.[29]

Interestingly, sample 30-20-90 has comparable elongation at break (*ca.* 1230%) and tensile strength (*ca.* 41MPa) to those of sample 40-0-0, while the tensile modulus is 1 fold higher. Besides, sample 30-20-90 has lower T_m (183 *vs.* 196°C) but higher $T_{5\%}$ (337 *vs.* 264°C) than sample 40-0-0 as showed in Table 2. These results clearly reveal that incorporation of small amount of CHDA as co-monomer for the modification of TPEE has similar effect on the tensile properties of the material, comparing to the conventional way of increasing soft segment. Nonetheless, our new strategy brings about better processibility and higher tensile modulus to the material. However, further replacement of aromatic ring with 100*mol*% of CHDA (sample 30-100-90) results in product with fairly low tensile modulus and strength but relatively improved elongation at break. This is due to the low degree of crystallinity of the hard segment of the sample.

Another interesting phenomena is observed for the manipulation of stereochemistry of CHDA. Samples 30-10-50 and 30-10-30 have less amount of *trans*-CHDA ratio in their molecular chain compared with 30-10-90, while the substitution percentage of CHDA over PTA is all around 10*mol*%. Decreasing the ratio of *trans*-CHDA, that is increasing the ratio of *cis*-CHDA, leads to increase of elongation at break as well as tensile strength without loss in tensile modulus. And at the same time, T_m decreases a little bit while $T_{5\%}$ remains unchanged. These results are in excellent agreement with our findings in polyester system.[29] The incorporation of *cis*-CHDA would break the stable crystalline domain formed by *trans*-CHDA, resulting in the releasing of intrinsic entropy elasticity of the molecular chain. In addition, we can further conclude that control over stereochemistry of CHDA has similar effect on the processibility and tensile properties of TPEE compared with simply adjusting the substitution amount of CHDA. And both methods are better than the conventional style which changes soft segment occupation ratio.

Elastic properties

The elastic properties of the obtained elastomers are investigated by cyclic tensile testing and the results are summarized in Table 4. The representative cyclic tensile testing strain-stress curves are shown in Figure 6. The elastic properties of materials refer to the ability of the materials to restore their original shape after certain amount of deformation under external stress. Samples with higher shape recovery ratio in the first cycle are considered to have better elastic property.[29] The increasing elasticity of traditional TPEEs results from soft segments.[37] Thus we observe significant increase of shape recovery ratio in the first cycle from 17.3 to

Table 4 Elastic property of PBCT-PTMG samples.[a]

Sample	$R_r(1)$ (%)	$R_r(2)$ (%)	$R_r(3)$ (%)	$R_r(4)$ (%)	$R_r(5)$ (%)
30-0-0	17.3±0.2	95.4±0.7	97.0±0.5	98.0±0.5	98.1±0.2
40-0-0	26.4±1.3	95.5±0.1	97.2±0.1	97.9±0.1	99.0±0.1
60-0-0	45.0±0.1	96.5±0.4	98.4±0.2	98.6±0.1	99.2±0.2
30-10-90	18.5±0.7	96.6±0.1	98.0±0.3	98.7±0.2	98.8±0.2
30-20-90	21.5±	92.2±	95.1±	96.8±	97.6±

	0.4	0.8	1.3	1.2	0.8
30-100-90	28.9±0.3	95.0±0.8	97.9±0.9	98.2±0.8	102.9±5.4
30-10-30	24.3±0.9	95.9±2.7	96.5±1.6	96.2±1.0	95.9±1.1
30-10-50	22.9±0.5	94.1±1.9	100±8.5	92.6±5.5	95.6±0.6

a) Elastic property is demonstrated by shape recovery ratio at 500% strain using cyclic tensile testing.

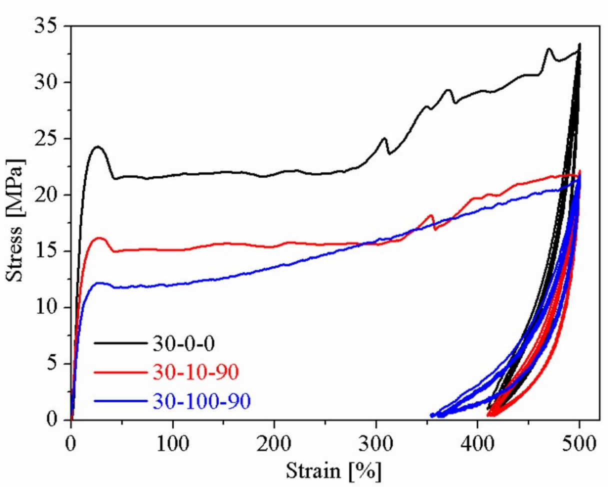


Figure 6 Representative cyclic tensile testing strain-stress curves of PBCT-PTMG samples

26.4 and 45.0% when the soft segment content increases from 30 to 40 and 60% (30-0-0 *vs.* 40-0-0 and 60-0-0), respectively. On the other hand, incorporation of small amount of CHDA has little impact on the elastic properties of PBCT-PTMG samples comparing to those of the samples with more amount of polyether soft segment. With 10 or 20*mol*% CHDA substitution amount, the shape recovery ratio in the first cycle increases slightly from 17.3 to 18.5 and 21.5% (30-0-0 *vs.* 30-10-90 and 30-20-90). Further increasing the substitution amount of CHDA to 100*mol*%, the shape recovery ratio in the first cycle reaches 28.9%, which is even higher than that of 40-0-0 (26.4%). This result reveals the “elastic” nature of the aliphatic ring in which it plays a role similar to that of polyether soft segment. The fully substituted sample (30-100-90) has poor tensile properties (*i.e.* low tensile modulus and strength) but relatively better elastic property. The “elastic” nature of the aliphatic ring is further reflected by varying the stereochemistry of CHDA unit. With more amount of *cis* isomer of CHDA, the PBCT-PTMG sample shows better elastic property. The shape recovery ratio in the first cycle increases from 18.5% to 22.9 and 24.3% when the *cis* isomer of CHDA increases from 10 to 50 and 70*mol*% (30-10-90 *vs.* 30-10-50 and 30-10-30). This observation is in good agreement with our previous finding in the soft-segment free polyester elastomer system.[29] The “elastic” nature of the aliphatic ring comes from its unique non-planar ring structure. The irregular *cis* isomer tends to form amorphous region and results in the break of crystalline domains so that the elastic property of the sample is enhanced. Nonetheless, addition of CHDA to produce PBCT-PTMG elastomers has only limited improvement on the elastic properties compared with conventional PBT-PTMG elastomers.

Conclusion

In conclusion, we have successfully performed a modification on traditional TPEEs which decreases their T_m while increases their $T_{5\%}$ without sacrificing their tensile property and elasticity. This modification is achieved by partially replacing aromatic ring structure with aliphatic one. The resulted PBCT-PTMG consists with two hard segments and two soft segments, PBT and PBC hard segments and PBT and PBC soft segments respectively. The incorporated PBC hard segment effectively decreases the T_m of the material while increases the thermal stability, resulting in better processibility. And the PBC soft segment makes substantial contribution to the improvement on the tensile strength and the elongation at break with only limited influence on the tensile modulus and elastic property. In addition, the regulation on the stereochemistry of the aliphatic ring structure further reveals its “elastic” nature. More importantly, our work provides a facile and effective way for the synthesis of novel thermoplastic elastomer with enhanced performance, which takes full advantage of aliphatic ring structure. We believe that this common yet unique structure has great potential for the fabrication of a series of novel materials with interesting and useful properties.

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Graphic Abstract

Incorporation of 1,4-cyclohexanedicarboxylic acid into poly(butylene terephthalate)-b-poly(tetramethylene glycol) to Alter Thermal Properties without Compromising Tensile and Elastic Properties

Fei Liu, Junwu Zhang, Jinggang Wang, Haining Na, Jin Zhu**

Incorporation of 1,4-cyclohexanedicarboxylic acid to partially replace terephthalic acid results in a thermoplastic elastomer with decreased melting temperature and increased thermal stability while tensile and elastic properties remain unchanged.