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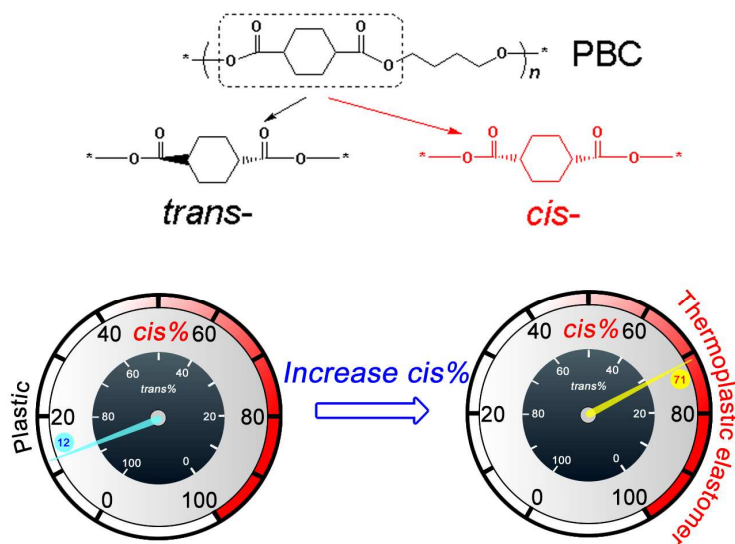
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Graphic Abstract

Soft Segment Free Thermoplastic Polyester Elastomers with High Performance

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Soft segment free thermoplastic polyester elastomer is fabricated by adjusting cis-1,4-cyclohexylene ring moiety in poly(butylene 1,4-cyclohexanedicarboxylate) from 12% to 71%.



Soft Segment Free Thermoplastic Polyester Elastomers with High Performance

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A soft segment free thermoplastic polyester elastomer is fabricated by controlling the stereochemical structure of molecular chain with the utilization of *cis* 1,4-cyclohexylene ring moiety (*cis*-CHRM) in poly(butylene 1,4-cyclohexanedicarboxylate) (PBC). PBC with 71% *cis*-CHRM exhibits well elasticity with shape recovery rates of 64% at 200% strain and 92% at break, tensile modulus, strength and elongation at break at 111 and 18MPa and 1230%, respectively.

Introduction

Thermoplastic elastomers (TPEs) are a particular class of polymeric materials that possess both the facile processability of plastic and the superior elasticity of rubber.¹ During the past decades, the traditional strategy to synthesize TPE is to introduce amorphous and flexible soft segments into thermoplastic polymer chains.

Soft segments form micro-phase separated structures in the TPE matrix, providing superior elasticity. This traditional strategy has allowed for the development of many types of TPEs such as styrenic thermoplastic elastomer (TPS),² thermoplastic polyurethane elastomer (TPU),^{3,4} thermoplastic poly(ether-amide) elastomer (TPAE)⁵ and thermoplastic poly(ether-ester) elastomer (TPEE).^{6,7}

However, it is not ideal to introduce soft segments to a thermoplastic polymer chain because it always inevitably brings about a decrease in thermal and tensile properties to the thermoplastic polymer.⁸ Therefore, it is interesting to develop an alternative methodology to synthesize TPEs without sacrificing their overall properties. As mentioned above, it is crucial not to introduce soft segment to TPEs in order to maintain good tensile and thermal properties. On the other hand, the use of soft segments to induce “soft” phases in the TPE matrix is a prerequisite to initiate superior elasticity. Thus the traditional strategy is not suitable for fabricating TPEs with high overall tensile and thermal properties. It is therefore necessary to develop an alternative way to gain elasticity without using soft segments. It is well-known that flexible polymer chains such as rubber and elastomer possess entropic elasticity and are able to recover their origin shape after large deformation. This property is exactly like the one soft segments play in traditional TPE. The only important difference between a plastic and a traditional TPE lies in the “soft” phases. This difference essentially suggests that a polymer with flexible chains can exhibit intrinsic elasticity if interactions between flexible chains are small. This inspires us to create a novel strategy to synthesize soft segment free TPEs by releasing the intrinsic elasticity of

polymer chains. Accordingly, high performance particularly high mechanical and thermal properties can be expected.

The most effective way to reduce intra-limitations between polymer chains is to introduce irregular structure. For example, polybutadiene (PB) can be either a plastic or a rubber, depending on its stereochemical structure. 1,3-butadiene can be polymerized to PB mainly in two ways, 1,4-*trans* and 1,4-*cis*.^{9,10} PB with a high amount of 1,4-*trans* butadiene moieties can easily crystallize because of its regular structure, resulting in strong interactions between polymer chains. On the other hand, PB with a high amount of irregular 1,4-*cis* butadiene moieties does not crystallize. The amorphous phases show properties of a synthetic rubber. The aim of this work is to simultaneously improve the rigidity and toughness of polymers by incorporating non-planar hexatomic rings to their chains. Hexatomic rings are relatively rigid and at the same time are able to exhibit two different stereochemical structures (*cis* and *trans*, which are irregular and regular, respectively) in the synthesis of polymers.¹¹⁻¹³ Accordingly, new TPEs containing non-planar hexatomic rings are expected.

The literature reported on the use of 1,4-cyclohexylene ring moiety (CHRM), especially *trans*-CHRM in the synthesis of thermoplastic polymers (particularly polyesters).¹³⁻¹⁹ As for poly(butylene 1,4-cyclohexanedicarboxylate) (PBC), *cis*-CHRM is rarely used.²⁰⁻²⁹ Therefore, only the properties of PBC as a plastic are studied.²⁴⁻²⁷ The effect of *cis*-CHRM on its elasticity has been ignored. In this communication, we discuss on the effect of *cis*-CHRM on the properties of PBC for the first time. By tuning the stereochemical structure of CHRM, a new soft segment

free TPE with high overall mechanical properties is proposed. Accordingly, a simple and effective strategy to synthesize soft segment free TPEs with high performance is established.

Experimental section

Synthesis: PBC were synthesized via a conventional melt polycondensation process from CHDA and BDO using titanium(IV) butoxide as a catalyst (Scheme 1).¹³ The PBC samples are denoted as PBC_x, where x is the amount of *cis*-CHRM in the polymer chain.

Characterization: Molecular weights and molecular weight distributions were measured on PL-GPC220 gel permeation chromatography (GPC). The structure and the amount of *cis*-CHRM in the polymer chains of PBC were determined by proton nuclear magnetic resonance (¹H NMR) in CDCl₃ 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). Dynamic mechanical analysis (DMA) was conducted with a METTLER-TOLEDO dynamic mechanical analyzer (DMA/SDTA861e) at a fixed frequency of 1 Hz, operated in the film tension mode. Tensile testing and cyclic tensile testing were performed in an Instron5567 tensile testing machine with a load cell of 500 N.

Detailed information about synthesis and characterization is provided in Electronic Supplementary Information (ESI)

Results and discussion

PBCs are synthesized via a convenient melt polycondensation process from 1,4-cyclohexanedicarboxylic acid (CHDA) with 1,4-butanediol (BDO) (Scheme 1). The amount of *cis*-CHRM in the final products ranges from 12 to 71% (Table 1), as determined by ^1H NMR (Figure 1). Deviation of the final compositions from the feed ones is observed due to the isomerization between *cis* and *trans* isomers at high temperature.³⁰ In fact the amount of *cis*-CHRM at thermodynamic equilibrium is 34%,¹⁷ and once it is not in this balanced state under high temperature, the isomerization is inevitable. The more deviation from the balanced state, the more isomerization will occur. Thus only 1% and 6% of isomerization are found for PBC36 and PBC44 respectively, but 11% and 26% of isomerization occurred for PBC12 and PBC71, respectively. All samples have similar number-average molecular weights (M_n) and molecular weight distribution (M_w/M_n) of about 30 000 and 2.5, respectively (Table 1). Thus differences in properties of PBC mainly depend on the amount of *cis*-CHRM.

PBC turns from a semicrystalline polymer to an amorphous one when the amount of *cis*-CHRM increases from 12 to 71% (Table 2). An interesting phenomenon is observed for PBC44, whose second heating scan shows cold crystallization and melting temperature (T_m) (Figure 2a), while the cooling scan does not show a crystallization temperature (T_c) (Figure 2b). This phenomenon indicates that when the amount of *cis*-CHRM increases from 12% to 44%, the irregular structure introduces more “kinks” into the polymer chain,¹³ which will hinder the

formation of crystalline by *trans*-CHRM when cooling from melt. However, a substantial amount of *trans*-CHRM in the polymer chain (56% for PBC44) can still induce a cold crystallization when the polymer chain is flexible at a temperature higher than the glass transition temperature. Thus the second heating scan of PBC44 shows cold crystallization and T_m . Given that both PBC12 and PBC36 have T_m and T_c , while PBC71 has no T_m , the transition of PBC from a semicrystalline polymer to an amorphous one should happen between 36% and 44%. Berti et al. found a value close to this range.¹³ Moreover, an increase in the amount of *cis*-CHRM results in a steady decrease in the glass transition temperature, as evidenced by both DSC (T_g) and DMA (T_α) (Table 2). Therefore, the incorporation of *cis*-CHRM plays a role in reducing the interactions among PBC chains and therefore their ability to crystallize.^{13,31} In addition, all PBC have high thermal stability regardless of the amount of *cis*-CHRM (Table 2), with $T_{5\%}$ around 380°C in N₂ and 365°C in air atmosphere, respectively.

The fact that PBC changes from a semicrystalline polymer to an amorphous one as the amount of *cis*-CHRM increases has a significant effect on its tensile properties. Table 3 shows tensile properties of PBC with different amounts of *cis*-CHRM and Figure 3 shows representative strain-stress curves. It is seen that all four samples show strain-stress curves for a typical thermoplastic polyester which consists of four regions:³² 1) linear and non-linear viscoelasticity, 2) neck region/strain softening, 3) plastic flow and 4) strain hardening. For the three semicrystalline samples, as the amount of *cis*-CHRM increases, χ_c decreases. Thus E and σ_y decreases whereas σ_t , ε_b and ε_y increase, as expected. On the other hand, it is interesting to note that the tensile

properties especially E of PBC71 and PBC12 are comparable except ϵ_b which differs greatly. It is 1230% and 520% for PBC 71 and PBC12, respectively. A higher ϵ_b is due to a larger amount of the amorphous region. A fully amorphous sample is expected to have a much higher ϵ_b than a semicrystalline one. However, due to the strain hardening effect,³³ PBC44 has the highest ϵ_b although the amount of amorphous region of PBC44 is smaller than that of PBC71.

The elastic properties of PBC are investigated by cyclic tensile testing. Table 4 shows the recovery rates of the cyclic tensile testing with 200% strain (R_T). When the amount of *cis*-CHRM increases from 12% to 71%, the first cycle recovery rate of PBC increases steadily from 11% to 64%, confirming the shift of PBC from a plastic to a TPE. The elastic property of PBC is also shown by the shape recovery rate at break (R_{tb}) (Table 4). The R_{tb} of PBC increases as the amount of *cis*-CHRM increases and reaches 92% with 71% *cis*-CHRM.

The high elasticity of traditional TPEs originates from soft segments.³⁴ It is like part of the polymer chains of a hard plastic are modified to become soft. The intrinsic entropic elasticity of hard segments are restrained due to high T_g or strong interactions between molecular chains such as crystallization and hydrogen bonding. Thus polymer chains are either frozen in a glassy state (*e.g.* polystyrene and PBT) or the chain mobility is restricted by strong interactions between polymer chains (*e.g.* polyamide and polyurethane). As a result, soft segments have to be incorporated by copolymerization or blending to introduce external entropic elasticity. In fact, it is

impossible for this type of modification to completely avoid the obvious decrease of mechanical modulus and strength.

By contrast, the strategy we have developed is to modify polymer chains in such a way that their intrinsic entropic elasticity can be fully released. The formation of an amorphous region by incorporation of irregular non-planar ring moieties into polymer chains promotes the effective release of the intrinsic entropic elasticity of PBC. Since PBC with full *trans*-CHRM is a semicrystalline plastic with T_g of 18°C,¹³ part of polymer chains are flexible and in their rubber-elastic state under room temperature but are restricted by the crystalline domains. Thus breaking the crystalline domains formed by *trans*-CHRM will release the intrinsic entropic elasticity and achieve the transition from a plastic to a TPE. Manipulation of stereochemistry, *i.e.*, partial replacement of *trans*-CHRM by *cis*-CHRM whose structure is irregular, successfully results in the shift of PBC from a plastic to a TPE. *cis*-CHRM not only plays a role as an irregular structure to break the crystalline domains but also decreases the T_g of the PBC. It is noteworthy that TPEs with intrinsic entropic elasticity are flexible amorphous materials. Instead of calling upon crystallization or strong interactions, they have chain entanglements which act as physical net points to prevent excessive chain slipping which would result in permanent deformation.^{33,34} In the case of PBC, chain entanglements not only prevent large permanent deformation upon an external stress (The permanent deformation at break of PBC with 71% *cis*-CHRM is only 8%), but also are responsible for the high E , which is even comparable to that of the semicrystalline PBC. Similar processes with the aim to alter the regularity of polymer

chains are the copolymerization of ethylene with vinyl acetate and to produce ethylene-vinyl acetate elastomer (EVA) and that of propylene (or a third diene monomer (DM)) to produce ethylene-propylene elastomer (EP or EPDM).

Another advantage of using non-planar ring moieties to synthesize TPEs is that it is possible to obtain both superior elasticity and high mechanical modulus and strength. Table 3 shows that E , σ_t and ε_b of PBC71 are as high as 111MPa, 18MPa and 1,230%, respectively. Their modulus and strength are much higher than those of a TPE obtained from the traditional strategy.^{8, 36-40}

Conclusions

In summary, we have developed a soft segment free strategy for the synthesis of high performance TPEs via the manipulation of stereochemistry for plastics with intrinsic entropic elasticity. By incorporation of irregular non-planar ring moieties to polymer chains, the crystalline region is disrupted and the intrinsic entropic elasticity is released. Comparing with TPEs obtained by the traditional strategy, the new strategy reported in this paper with the manipulation of stereochemistry of CHRM is much simpler and more effective to achieve soft segment free TPEs with high overall mechanical and thermal properties. More importantly, our research provides a new guideline for the synthesis of TPEs from plastics based on the release of the intrinsic entropic elasticity from their polymer chains.

Acknowledgements

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Figure captions

Scheme 1. Synthesis of PBC from CHDA and BDO.

Figure 1. ^1H NMR spectra (CDCl_3 , 400MHz) of PBC.

Figure 2. DSC curves for PBC in the (a) second heating and (b) cooling scans.

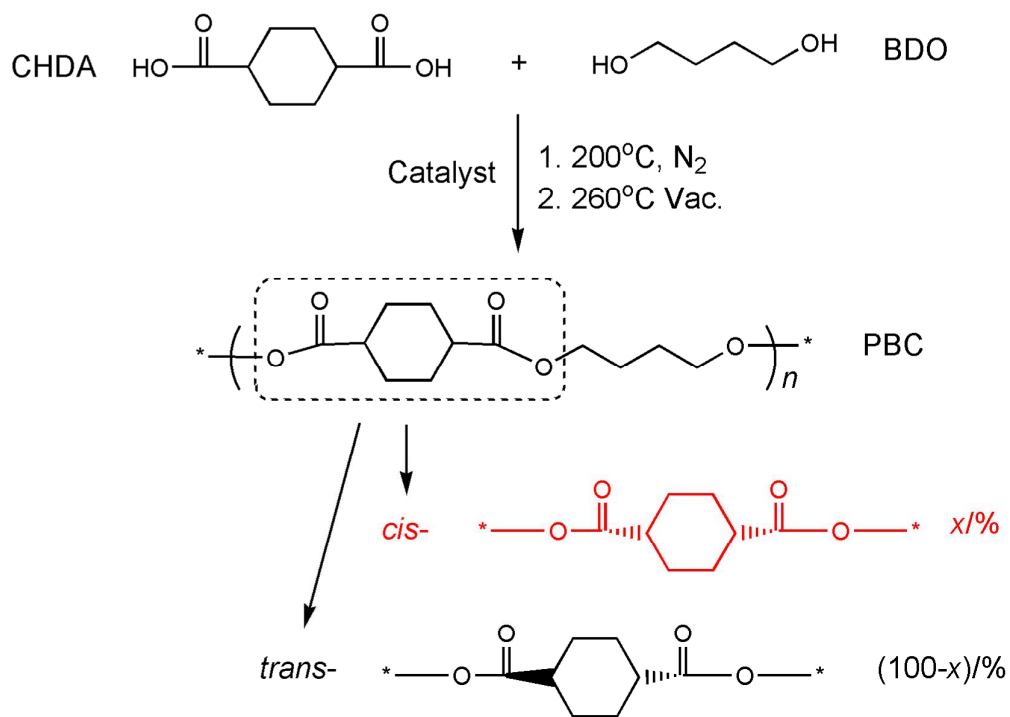
Figure 3. Representative tensile strain-stress curves of PBC.

Table 1. Composition and molecular weight of PBC.

Table 2. Thermal properties of PBC.

Table 3. Tensile properties of PBC.

Table 4. Elastic properties of PBC.



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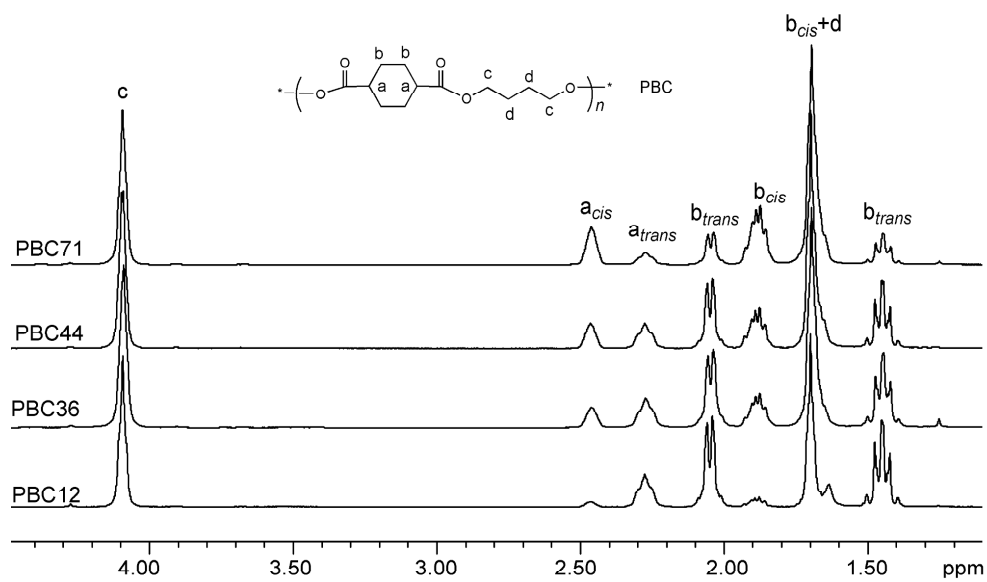


Figure 1. ¹H NMR spectra (CDCl₃, 400MHz) of PBC.

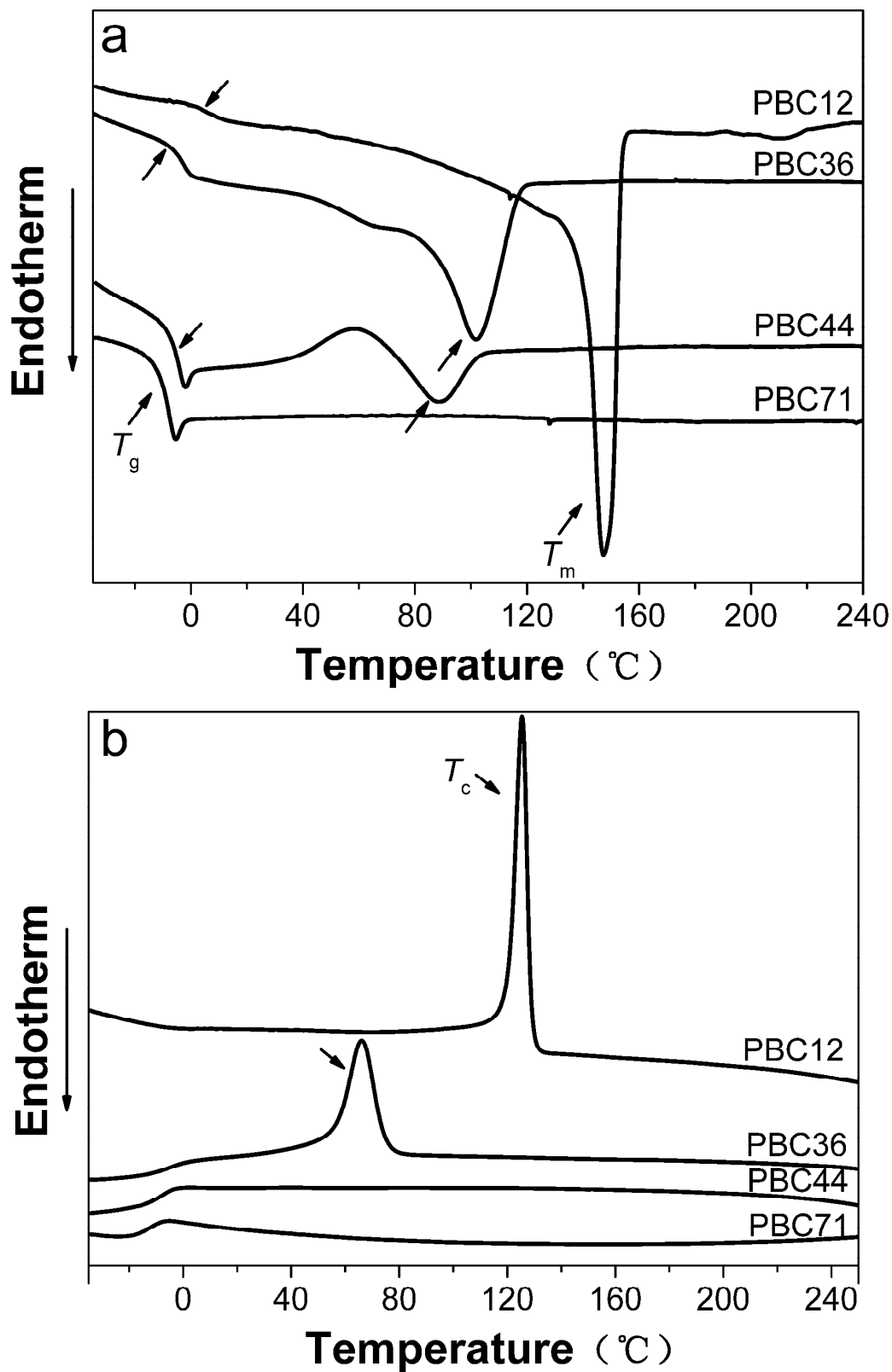


Figure 2. DSC curves for PBC in the (a) second heating and (b) cooling scans.

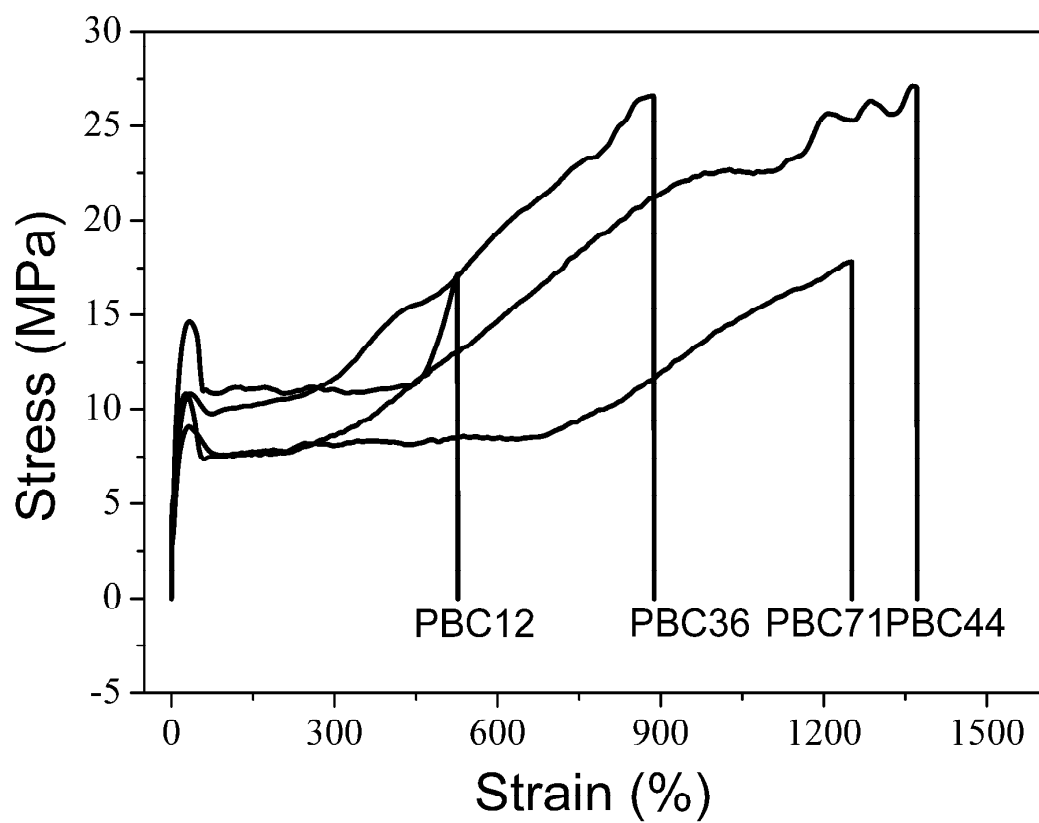


Figure 3. Representative tensile strain-stress curves of PBC.

Table 1. Composition and molecular weight of PBC.

Sample	<i>cis</i> -CHRM%		M_n^c	M_w/M_n^c
	Feed ^a	Final ^b		
PBC12	1	12	33 000	2.5
PBC36	37	36	30 000	2.1
PBC44	50	44	30 000	2.2
PBC71	97	71	30 000	2.5

a 99% *trans*-CHDA, *mix*-CHDA (*cis/trans* 50/50) and 97% *cis*-CHDA were used as starting materials for PBC12, PBC44 and PBC71, respectively, and a mixture of 99% *trans*-CHDA and *mix*-CHDA was used as a starting material for PBC36; b calculated from ¹H NMR in CDCl₃ based on the integration of signals at 2.47ppm and 2.28ppm, which could be assigned to the protons of -CH- in *cis*- and *trans*-CHRM, respectively;¹³ c determined by GPC in CHCl₃;

Table 2. Thermal properties of PBC.

Sample	T_m^a [°C]	T_c^a [°C]	χ_c^a [%]	T_g^a [°C]	T_α^b [°C]	$T_{5\%}^c$ [°C]	
						N ₂	Air
PBC12	147	125	19.4	5.0	27.5	382	370
PBC36	102	66	18.7	-4.0	7.5	380	363
PBC44	89	/	10.7	-4.5	7.5	380	363
PBC71	/	/	0.0	-8.0	5.0	378	365

a Determined by DSC, T_m , melting temperature, T_c , crystallization temperature, χ_c , degree of crystallinity and T_g , glass transition temperature; b Determined by DMA (Figure S1 and S2), T_α , α transition temperature; c Determined by TGA, $T_{5\%}$, temperature at which the weight loss is 5%.

Table 3. Tensile properties of PBC.^a

Sample	E [MPa]	σ_t [MPa]	ε_b [%]	σ_y [MPa]	ε_y [%]
PBC12	157±7	17±1	520±7	14±1	21±1
PBC36	99±10	27±1	880±17	11±0.4	26±4
PBC44	81±12	28±1	1 360±28	9±1	28±2
PBC71	111±12	18±1	1 230±35	11±0.4	26±1

a Determined by tensile testing, Young's modulus (E), tensile strength (σ_t), elongation at break (ε_b), stress at yield (σ_y), and strain at yield (ε_y)

Table 4. Elastic properties of PBC.^a

Sample	$R_r(1)$ [%]	$R_r(2)$ [%]	$R_r(3)$ [%]	$R_r(4)$ [%]	$R_r(5)$ [%]	R_{rb} [%]
PBC12	11±1	95±2	97±1	100±2	100±5	38
PBC36	35±1	93±3	96±1	97±1	100±2	53
PBC44	41±2	91±1	96±2	98±1	99±1	68
PBC71	64±4	96±2	97±2	99±1	100±1	92

^a The recovery rate at 200% strain ($R_r(N)$) for the Nth cycle in the cyclic tensile testing and the recovery rate at break (R_{rb}).