High-Performance Soft-Segment-Free Thermoplastic Polyester Elastomers: Postprint

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Abstract

A soft segment free thermoplastic polyester elastomer is fabricated by controlling the stereochemical structure of molecular chains with the utilization of the cis 1,4-cyclohexylene ring moiety (cis-CHRM) in poly(butylene 1,4-cyclohexanedicarboxylate) (PB

Full Text

Preamble

Soft Segment-Free Thermoplastic Polyester Elastomers with High Performance†

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A soft segment-free thermoplastic polyester elastomer was fabricated by controlling the stereochemical structure of molecular chains through the incorporation of the cis-1,4-cyclohexylene ring moiety (cis-CHRM) in poly(butylene 1,4-cyclohexanedicarboxylate) (PBC). PBC containing 71% cis-CHRM exhibited excellent elasticity with shape recovery rates of 64% at 200% strain and 92% at break, along with a tensile modulus of 111 MPa, tensile strength of 18 MPa, and elongation at break of 1230%.

Introduction

Thermoplastic elastomers (TPEs) represent a unique class of polymeric materials that combine the facile processability of plastics with the superior elasticity of rubber [?]. Over the past few decades, the conventional strategy for synthesizing TPEs has involved introducing amorphous, flexible soft segments into thermoplastic polymer chains. These soft segments form microphase-separated structures within the TPE matrix, providing enhanced elasticity. This approach has enabled the development of various TPE families, including styrenic thermoplastic elastomers (TPSs) [?], thermoplastic polyurethane elastomers (TPUs) [?, ?], thermoplastic poly(ether-amide) elastomers (TPAEs) [?], and thermoplastic poly(ether-ester) elastomers (TPEEs) [?, ?].

However, incorporating soft segments into thermoplastic polymer chains is inherently problematic as it inevitably compromises the thermal and mechanical properties of the material [?]. Therefore, developing alternative methodologies to synthesize TPEs without sacrificing overall performance represents an important research direction. As discussed above, avoiding soft segments in TPEs is crucial for maintaining excellent tensile and thermal properties. Conversely, using soft segments to induce "soft" phases in the TPE matrix remains a prerequisite for achieving superior elasticity. This fundamental contradiction renders the traditional strategy unsuitable for fabricating TPEs with high combined tensile and thermal performance. Consequently, novel approaches that confer elasticity without relying on soft segments are necessary.

It is well established that flexible polymer chains in rubbers and elastomers possess entropic elasticity, enabling recovery from large deformations. This behavior mirrors that of soft segments in conventional TPEs. The critical distinction between a plastic and a traditional TPE essentially lies in the presence of these "soft" phases, suggesting that polymers with flexible chains can exhibit intrinsic elasticity if interchain interactions are sufficiently weak. This insight inspires a novel strategy for synthesizing soft segment-free TPEs by unlocking the intrinsic elasticity of polymer chains, which should yield high performance, particularly in mechanical and thermal properties.

The most effective method for reducing interchain limitations involves introducing irregular structures. For example, polybutadiene (PB) can function as either a plastic or rubber depending on its stereochemical structure. 1,3-Butadiene polymerizes primarily via two pathways: 1,4-trans and 1,4-cis [?, ?]. PB rich in 1,4-trans units readily crystallizes due to its regular structure, resulting in strong interchain interactions. In contrast, PB containing predominantly irregular 1,4-cis units does not crystallize, with the amorphous phases exhibiting synthetic rubber properties. This work aims to simultaneously enhance polymer rigidity and toughness by incorporating non-planar six-membered rings into polymer chains. Such rings are relatively rigid yet can adopt two distinct stereochemical configurations (irregular cis and regular trans) during polymer synthesis [?], enabling the design of new TPEs containing non-planar hexatomic rings.

Previous literature has reported the use of the 1,4-cyclohexylene ring moiety (CHRM), particularly the trans isomer, in thermoplastic polymer synthesis (especially polyesters) [?]. However, the cis-CHRM has rarely been utilized in poly(butylene 1,4-cyclohexanedicarboxylate) (PBC) [?], and research has focused exclusively on PBC as a plastic material [?]. The effect of cis-CHRM on elasticity has been overlooked. In this communication, we investigate for the first time the influence of cis-CHRM on PBC properties. By tuning the stereochemical structure of CHRM, we propose a new soft segment-free TPE with high overall mechanical performance, establishing a simple and effective strategy for synthesizing high-performance TPEs without soft segments.

Experimental Section

Synthesis

PBC was synthesized via conventional melt polycondensation from 1,4-cyclohexanedicarboxylic acid (CHDA) and 1,4-butanediol (BDO) using titanium(IV) butoxide as a catalyst (Scheme 1). The PBC samples are denoted as PBCx, where x represents the percentage of cis-CHRM units in the polymer chain.

Characterization

Molecular weights and molecular weight distributions were measured using a PL-GPC220 gel permeation chromatograph (GPC). The polymer structure and cis-CHRM content were determined by proton nuclear magnetic resonance (^{1H} NMR) in $CDCl_3$ using a Bruker AVIII400 spectrometer at room temperature. Differential scanning calorimetry (DSC) was performed on a Mettler-Toledo DSC I. Thermal stability was evaluated using a Mettler-Toledo TGA/DSC thermogravimetric analyzer (TGA). Dynamic mechanical analysis (DMA) was conducted with a Mettler-Toledo DMA/SDTA861e at a fixed frequency of 1 Hz in film tension mode. Tensile testing and cyclic tensile testing were performed on an Instron 5567 tensile testing machine equipped with a 500 N load cell. Detailed experimental procedures are provided in the ESI.†

Results and Discussion

PBCs were synthesized via convenient melt polycondensation from CHDA and BDO (Scheme 1). The cis-CHRM content in the final products ranged from 12% to 71% (Table 1), as determined by ^{1H} NMR (Fig. 1 [Figure 1: see original paper]). Deviations between final compositions and feed ratios were observed due to cis-trans isomerization at elevated temperatures [**?**]. The thermodynamic equilibrium cis-CHRM content is 34% [**?**], and isomerization becomes significant when deviating from this equilibrium. Consequently, only 1% and 6% isomerization occurred for PBC36 and PBC44, respectively, whereas 11% and 26% isomerization were observed for PBC12 and PBC71, respectively. All samples exhibited similar number-average molecular weights (Mn) and polydispersities (Mw/Mn) of approximately 30,000 and 2.5, respectively (Table 1), ensuring that property differences primarily reflect variations in cis-CHRM content.

PBC transitioned from a semicrystalline to an amorphous polymer as the cis-CHRM content increased from 12% to 71% (Table 2). An interesting phenomenon was observed for PBC44: its second heating scan exhibited cold crystallization and a melting temperature (Tm) (Fig. 2a [Figure 2: see original paper]), while the cooling scan showed no crystallization temperature (Tc) (Fig. 2b). This indicates that increasing cis-CHRM content from 12% to 44% introduces more "kinks" into the polymer chain [?], which hinder crystalline domain formation by trans-CHRMs during cooling from the melt. However, the substantial trans-CHRM content (56% for PBC44) can still induce cold crystallization when polymer chains become flexible above the glass transition temperature, resulting in Tm during the second heating scan. Since both PBC12 and PBC36 exhibit Tm and Tc while PBC71 shows no Tm, the semicrystalline-to-amorphous transition occurs between 36% and 44% cis-CHRM content, consistent with values reported by Berti et al. [?]. Furthermore, increasing cis-CHRM content steadily decreased the glass transition temperature, as evidenced by both DSC (Tg) and DMA (Ta) (Table 2). Therefore, cis-CHRM incorporation reduces interchain interactions and crystallization ability [?, ?]. All PBCs demonstrated high thermal stability regardless of cis-CHRM content (Table 2), with 5% weight loss temperatures (T5%) around 380 °C in nitrogen and 365 °C in air.

The semicrystalline-to-amorphous transition significantly affected tensile properties. Table 3 summarizes the tensile properties of PBC with varying cis-CHRM content, and Fig. 3 [Figure 3: see original paper] shows representative stress-strain curves. All four samples exhibited typical thermoplastic polyester behavior with four distinct regions: (1) linear and nonlinear viscoelasticity, (2) necking/strain softening, (3) plastic flow, and (4) strain hardening [?]. For the three semicrystalline samples, increasing cis-CHRM content decreased yield stress and crystallinity while increasing elongation at break, as expected. Interestingly, the tensile properties, particularly Young' s modulus, of PBC71 and PBC12 were comparable, except for elongation at break, which differed substantially (1230% for PBC71 versus 520% for PBC12). The higher elongation at break for PBC71 reflects its greater amorphous content. However, due to strain hardening effects [?], PBC44 exhibited the highest elongation at break despite having less amorphous content than PBC71.

Cyclic tensile testing revealed the elastic properties of PBC (Table 4). As cis-CHRM content increased from 12% to 71%, the first-cycle recovery rate at 200% strain (Rr) steadily increased from 11% to 64%, confirming the transition from plastic to TPE behavior. The shape recovery rate at break (Rrb) also increased with cis-CHRM content, reaching 92% for PBC71.

The high elasticity of conventional TPEs originates from soft segments [?], which effectively modify portions of rigid polymer chains to become flexible. The intrinsic entropic elasticity of hard segments is typically constrained by high glass transition temperatures or strong interchain interactions such as crystallization and hydrogen bonding, leaving polymer chains either frozen in a glassy state (e.g., polystyrene, PBT) or with restricted mobility (e.g., polyamide, polyurethane). Consequently, soft segments must be incorporated via copolymerization or blending to introduce external entropic elasticity, inevitably compromising mechanical modulus and strength.

In contrast, our strategy modifies polymer chains to fully release their intrinsic entropic elasticity. Incorporating irregular non-planar ring moieties disrupts crystalline regions and promotes release of PBC' s intrinsic entropic elasticity. Since PBC with 100% trans-CHRM is a semicrystalline plastic with a Tg of 18 °C [**?**], portions of the polymer chains are flexible and rubbery at room temperature but constrained by crystalline domains. Disrupting these trans-CHRM crystalline domains releases the intrinsic entropic elasticity, enabling the plastic-to-TPE transition. Stereochemical manipulation through partial replacement of regular trans-CHRM with irregular cis-CHRM successfully achieves this transition. The cis-CHRM serves dual functions: as an irregular structure that disrupts crystalline domains and as a modifier that reduces Tg. Notably, TPEs with intrinsic entropic elasticity are flexible amorphous materials where chain entanglements, rather than crystallization or strong interactions, act as physical crosslinks to prevent excessive chain slip and permanent deformation [**?**, **?**]. For PBC, chain entanglements not only limit permanent deformation (only 8% permanent deformation at break for PBC71) but also maintain high modulus comparable to semicrystalline PBC. Similar strategies involving chain regularity modification include copolymerization of ethylene with vinyl acetate to produce EVA elastomers and copolymerization of propylene with diene monomers to produce EP/EPDM elastomers.

An additional advantage of using non-planar ring moieties for TPE synthesis is the simultaneous achievement of superior elasticity with high mechanical modulus and strength. Table 3 shows that PBC71 possesses a Young' s modulus of 111 MPa, tensile strength of 18 MPa, and elongation at break of 1230%—values significantly higher than those of TPEs prepared by conventional strategies [**?**, **?**].

Conclusions

In summary, we have developed a soft segment-free strategy for synthesizing high-performance TPEs through stereochemical manipulation of plastics with intrinsic entropic elasticity. Incorporating irregular non-planar ring moieties disrupts crystalline regions and releases intrinsic entropic elasticity. Compared with conventional TPE synthesis, this stereochemical manipulation of CHRMs provides a simpler and more effective route to soft segment-free TPEs with high overall mechanical and thermal properties. More importantly, this research establishes new guidelines for TPE synthesis from plastics based on releasing intrinsic entropic elasticity from polymer chains.

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References

1. R. J. Spontak and N. P. Pate, Curr. Opin. Colloid Interface Sci., 2000, 5, 334.
2. H. Schmalz, A. Bo, R. Lange and G. Krausch, Macromolecules, 2001, 34, 8720.
3. L. Zhang, Y. Jiang, Z. Xiong, X. Liu, H. Na, R. Zhang and J. Zhu, J. Mater. Chem. A, 2013, 1, 3263.
4. R. Yu, L. Zhang, Y. Feng, R. Zhang and J. Zhu, Chin. J. Polym. Sci., 2014, 32, 1099.
5. N. J. Sijbrandi, A. J. Kimenai, E. P. C. Mes, R. Broos, G. Bar, M. Rosenthal, Y. Odarchenko, D. A. Ivanov, P. J. Dijkstra and J. Feijen, Macromolecules, 2012, 45, 3948.
6. J. G. Drobny, Handbook of Thermoplastic Elastomers, William Andrew Publishing, 2007, p. 249.
7. A. A. Deschamps, D. W. Grijpma and J. Feijen, Polymer, 2001, 42, 9335.
8. N. M. T. Pires, F. M. B. Coutinho and M. S. Costa, Eur. Polym. J., 2004, 40, 2599.
9. L. P. Chen, A. F. Yee, J. M. Goetz and J. Schaefer, Macromolecules, 1998, 31, 5371.
10. C. Berti, A. Celli, P. Marchese, E. Marianucci, G. Barbiroli and F. Di Credico, Macromol. Chem. Phys., 2008, 209, 1333.
11. C. Berti, A. Celli, P. Marchese, E. Marianucci, S. Sullalti and G. Barbiroli, Macromol. Chem. Phys., 2010, 211, 1559.
12. A. Celli, P. Marchese, S. Sullalti, C. Berti and G. Barbiroli, Macromol. Chem. Phys., 2011, 212, 1524.
13. B. Vanhaecht, B. Rimez, R. Willem, M. Biesemans and C. E. Koning, J. Polym. Sci., Part A: Polym. Chem., 2002, 40, 3720.
14. H. R. Kricheldorf and G. Schwarz, Makromol. Chem., 1987, 188, 1281.
15. C. Berti, E. Binassi, A. Celli, M. Colonna, M. Fiorini, P. Marchese, E. Marianucci, M. Gazzano, F. D. I. Credico and D. J. Brunelle, J. Polym. Sci., Part B: Polym. Phys., 2008, 46, 619.
16. M. Colonna, C. Berti, E. Binassi, A. Celli, M. Fiorini, P. Marchese, M. Messori and D. J. Brunelle, Polym. Int., 2011, 60, 1607.
17. M. Gigli, N. Lotti, M. Vercellino, L. Visai and A. Munari, Mater. Sci. Eng., C, 2014, 34, 86.
18. M. Gigli, N. Lotti, M. Gazzano, V. Siracusa, L. Finelli, A. Munari and M. D. Rosa, Polym. Degrad. Stab., 2014, 105, 210.
19. M. Gigli, N. Lotti, M. Gazzano, V. Siracusa, L. Finelli, A. Munari, M. D. Rosa, I. Industriale, U. Catania and V. A. Doria, Ind. Eng. Chem. Res., 2013, 52, 12876.
20. L. Wang, Z. Xie, X. Bi, X. Wang, A. Zhang, Z. Chen, J. Zhou and Z. Feng, Polym. Degrad. Stab., 2006, 91, 2220.
21. T. E. Sandhya, C. Ramesh and S. Sivaram, Macromolecules, 2007, 40, 6906.
22. B. Vanhaecht, M. N. Teerenstra, D. R. Suwier, R. Willem, M. Biesemans

and C. E. Koning, J. Polym. Sci., Part A: Polym. Chem., 2001, 39, 833.

23. J. A. Mason and R. W. Hertzberg, CRC Crit. Rev. Macromol. Sci., 1973, 1, 433.
24. Q. Liu, L. Jiang, R. Shi and L. Zhang, Prog. Polym. Sci., 2012, 37, 715.
25. E. V. Konyukhova, V. M. Neverov, Y. K. Godovsky, S. N. Chvalun and M. Soliman, Macromol. Mater. Eng., 2002, 287, 250.
26. A. Szymczyk, E. Senderek, J. Nastalczyk and Z. Roslaniec, Eur. Polym. J., 2008, 44, 436.
27. J. Zhang, F. Liu, J. Wang, H. Na and J. Zhu, Chin. J. Polym. Sci., 2015, DOI: 10.1007/s10118-015-1673-4.

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