One-Pot Synthesis of Supertough, Sustainable Polyester Thermoplastic Elastomers Using Block-Like, Gradient Copolymer as Soft Midblock

Wuchao Zhao¹, Chengkai Li¹, Xiao Yang², Jianghua He¹, Xuan Pang³, Yuetao Zhang¹*, Yongfeng Men²* & Xuesi Chen³*

¹State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun, Jilin 130012, ²State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, ³Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022

*Corresponding authors: ytzhang2009@jlu.edu.cn; men@ciac.ac.cn; xschen@ciac.ac.cn

Cite this: CCS Chem. 2021, 3, 1522-1531

It remains challenging to synthesize supertough thermoplastic elastomers (TPEs) since the stretchability and tensile strength are mutually exclusive. Here, we report a one-pot strategy for the preparation of sustainable, triblock polyester TPEs consisting of poly(ε-lactide) (PLLA) hard segments and poly(ε-caprolactone)-co-poly(δ-valerolactone) (PCVL) soft segments. The TPEs were synthesized successfully with high stretchability (up to 2100%) and strong tensile strength (up to 71.5 MPa) without requiring specific functionalized groups by simply adjusting the polymer microstructures, which, in turn, exhibited a world’s record toughness of 445 MJ/m³. Systematic investigation revealed that the block-like, gradient microstructure of PCVL improved the ductility by providing a flexible elastic network and enhancing the tensile strength through strain-induced crystallization. The practicability of this strategy was well demonstrated by lifting a water tank over 30,000 times heavier than itself and easy scale-up experiments.

Keywords: living polymerization, strain-induced crystallization, supertough, sustainable polyester, thermoplastic elastomers

Introduction

High-performance thermoplastic elastomers (TPEs), especially supertough TPEs with both high stretchability and strong tensile strength, have attracted much intense attention due to their wide applications in both engineering and biomedical fields.¹⁻⁶ So far, the development of supertough materials to attain both tensile strength and stretchability has traditionally been a compromise between hardness and ductility since these properties are generally mutually exclusive.⁷,⁸ Increasing the tensile strength is often achieved at the expense of elasticity and vice versa. To enhance the mechanical performance, several effective methods have been applied to the TPEs syntheses through smart design and precise synthesis, making remarkable progress of achieving toughness up to 387 MJ/m³, with characteristics such as filler-reinforcement,⁹,¹⁰ double networks of two components
blends, multicomponent cross-linking, and biomimetic strategy based on multiple hydrogen bonds. Clearly, introducing specific functionalized groups is essential for the toughening of elastomers. Without these reinforcement strategies, it seems an impossible mission to synthesize TPEs with both high stretchability and strong tensile strength.

ABA triblock (A-B-A-type copolymer) TPEs, composed of the hard end block A and soft midblock B, primarily the biorenewable and biodegradable polyester-based TPEs, have been widely used in the industrial field, medical science, and as traditional commodities, due to their ubiquitous biodegradable, renewable, and biocompatible properties. Several research groups have made significant contributions to this field and have pioneered a series of aliphatic polyesters TPEs with impressive mechanical properties. Typically, poly(lactide) (PLA), poly(cyclohexene-alt-phthalate), or poly(ε-methylene-γ-butyrolactone) served as hard end block A, whereas poly(ε-caprolactone) (PCL), poly(δ-valerolactone) (PVL), poly(menthine), and their homologs, or random copolymers with reduced crystallinity, acted as soft middle block B, respectively. Furthermore, multiblock polyesters, cross-linking polyesters, and end-functionalized polyesters were also reported to achieve TPEs with improved mechanical performance. So far, the reported polyester-based TPEs might exhibit either high elongation at break, up to 2100%, or tensile strength of ~37 MPa (Figure 1a); it remains an enormous challenge to prepare TPEs with both high stretchability and strong mechanical strength of the above-mentioned order of magnitude.

In this context, an organomagnesium complex was combined with 1,4-benzenedimethanol (BDM) initiator to prepare a series of triblock polyester TPEs consisting of poly(ε-lactide) (PLLA) hard segments and homopolymer (PCL or PVL) or copolymer poly(ε-caprolactone)-co-poly(δ-valerolactone) (PCVL) soft segment, from the living/controlled ring-opening polymerization (ROP) of renewable lactones. By changing the monomer feed ratio, the contents of soft or hard segments in TPEs are easily adjustable, thus, furnishing high-performance polyester TPEs with high elongation at break (up to 2100%) and strong tensile strength (up to 71.5 MPa) (Figure 1a). Further, systematic characterizations of these fabricated TPEs by differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR), small-angle X-ray scattering (SAXS), and wide-angle X-ray diffraction (WAXD), in comparison with control experiments, revealed that the block-like, gradient polyester PCVL played an essential role in toughening of TPEs. To the best of our knowledge, this is the first time a polyester TPE had been generated with a world’s record toughness of 445 MJ/m³, achieved successfully from the ROP of traditional cyclic lactones by simply adjusting the composition and microstructure of polymers.

**Experimental Section**

**General information**

All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, a high-vacuum line, or an argon-filled glovebox. Benzyl alcohol (BnOH) and "Bu₂Mg were purchased from J&K Scientific Ltd., and tetrahydrofuran (THF) [high-performance liquid chromatography (HPLC) grade] was purchased from Sigma (Shanghai, China). N,N,N′-trimethylhexamethylenediamine, hydrobromic acid, BDM, 2,4-di-tert-butylphenol, and ε-lactide (LLA) were purchased from Energy Chemical Co., Ltd. (Shanghai, China). All chemicals were used as received unless otherwise specified as follows. ε-Caprolactone (ε-CL; J&K Scientific Ltd., Beijing, China) and δ-valerolactone (δ-VL; Adamas-beta, Shanghai, China) were dried over CaH₂, distilled under nitrogen, and stored in a glovebox at...
–35 °C. Toluene (TOL) and benzene were refluxed over sodium/potassium alloy, followed by distillation under a nitrogen atmosphere; hexane and dichloromethane were refluxed over CaH₂, followed by distillation under nitrogen atmosphere. All solvents were stored over molecular sieves of 4 Å.

**General polymerization procedures**

Polymerizations were performed in 60 mL glass reactors inside the glovebox for runs carried out at room temperature (RT). In a typical polymerization procedure, a predetermined amount of Mg(II) complex solution and BnOH or BDM initiator were first mixed in TOL for 2 min. A 200 molar equiv of monomer e-CL (0.50 M in TOL) was added to the mixture inside a glovebox. After the first batch of monomers had reached total consumption, a 25 molar equiv of HMA (0.25 M in dichloromethane (DCM)) was added without quenching. After a measured time interval, a 0.2 mL aliquot was taken from the reaction mixture with a syringe and quickly quenched into a 4-mL vial containing 0.6 mL of undried “wet” CDCl₃ stabilized by 250 ppm of Butylated hydroxytoluene (BHT-H); the quenched aliquots were later analyzed by ¹H NMR to obtain the percent monomer conversion data. After the polymerization was stirred for the stated reaction time, the polymer was immediately precipitated by 200 mL of hexane, stirred for 1 h, filtered, washed with hexane, and dried in a vacuum oven at 50 °C overnight to constant weight.

**Polymer characterizations**

NMR spectra were recorded on Bruker Avance II 500 (Zurich, Switzerland, 500 MHz, ¹H; 126 MHz, ¹³C) instrument at RT in CDCl₃. Gel permeation chromatography (GPC) analyses were performed on a Waters 1515 instrument (Milford, MA) equipped with a guard column MIXED 7.5 × 50 mm PL column and two MIXED-C 7.5 × 300 columns and a differential refractive index (DRI) detector using THF (HPLC grade) as the eluent at 35 °C with a flow rate of 1 mL/min. The weight–average molar masses (Mₐ) and molecular weight distribution (MWD) (Mₙ/Mₚ) of the polymer samples were determined by WYATT DAWAN 8+ light scattering detector (LS) at 35 °C and a flow rate of 1 mL/min. The DRI increment (dn/dc) value of 0.084 mL/g was used for PVL and 0.076 mL/g for PCL, and 0.042 mL/g for PLA. Chromatograms were processed with Waters Breeze 2 software. Thermal properties were measured on a TA Instruments (New Castle, DE) Discovery DSC series DSC 25. Polymer samples were first heated to 200 °C at 10 °C/min, equilibrated at this temperature for 2 min, then cooled down to −80 °C at 10 °C/min, held at this temperature for 2 min, and then reheated to 200 °C at 10 °C/min. SAXS experiments were performed on the BL16B1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF) at RT. The wavelength of the X-rays was 0.932 Å, and two-dimensional (2D) SAXS patterns were recorded using a MAR-CCD detector (Norderstedt, Germany) at a sample-to-detector distance of 5745 mm. All 2D figures were transformed to one-dimensional (1D) curves via Fit2D software (https://www.esrf.fr/computing/scientific/Fit2D/). WAXD was performed on a customized microfocus WAXD system. A focused Cu Kα X-ray source (GeniX³⁰, Xenocs SA, Isère, France), generated at 50 kV and 0.6 mA and employed in this setup. The wavelength of X-ray radiation is 0.154 nm. 2D WAXD patterns were collected by a semiconductor detector with a resolution of 487 pixels × 195 pixels (pixel size = 172 µm) (Pilatus 100 K, DECTRIS AG, Baden, Switzerland) at a sample-to-detector distance of 45.8 mm. Each WAXD pattern was background corrected according to standard procedure utilizing the “Fit2DOO” program.³⁷ Atomic force microscopy (AFM) test was performed on Bruker Dimension FastScan (Karlsruhe, Germany), and the sample films were prepared by solvent vapor annealing.

TPE films (thickness ~150–300 µm) were prepared by dissolving triblock copolymers in chloroform and casting them on a glass plate. Then the solvent was allowed to evaporate for 24 h at RT, followed by removing the residual solvent under vacuum for 24 h. Dog-bone-shaped specimens were die-cut from the prepared films with a width of 2.0 mm and a length of 12 mm. Uniaxial tensile tests were conducted on an Instron universal testing machine (Model 5944; Cambridge, MA) equipped with a 2 kN load cell operated at a crosshead speed of 15 mm/min. Tests were performed at RT, and at least three measurements were performed for each sample. Toughness was calculated as the integral area under the stress–strain curve according to eq. 1.³⁸

\[
\text{Toughness} = \int_{\text{strain} = 0}^{\text{strain} = \text{str}} \text{(stress)} \, d(\text{strain})
\]

where stress, tensile stress, MPa; strain, the tensile strain was expressed as a percentage (%).

The true strain: \( \epsilon = \ln \frac{l}{l_0} = \ln \frac{\Delta l + l_0}{l_0} = \ln(1 + \epsilon) \) (2)

where \( l \), tensile length; \( l_0 \), initial length.

The true stress: \( \sigma = \frac{P}{S_0} = \frac{P}{S_0}(1 + \epsilon) \) (3)

where, \( P \), load, N; \( S_0 \), initial area, m².

**Results and Discussion**

**Synthesis of ABA triblock polyester TPEs**

To synthesize triblock polyester TPEs, it is highly demanded to develop more efficient polymerization systems. Based on our previous experiences,³⁹–⁴¹ a new butylmagnesium 2,4-di-tert-buty1-6-((methyl(2-(methylamino)ethyl)amino)methyl)phenolate (Mg(II))
was synthesized and combined with BnOH to promote living/controlled ROP of renewable cyclic lactones (see Supporting Information Table S1 and Figure S1). The living nature of this Mg(II)/BnOH system was verified by successful synthesis of well-defined diblock polymer PCL-β-PLLA, revealed by GPC analysis (see Supporting Information Figure S2b) and NMR spectroscopy (see Supporting Information Figures S5 and S6). PLA is known to be a perfect hard segment candidate for TPEs synthesis due to its biorenewable, biocompatible and biodegradable properties, as well as high stiffness,\textsuperscript{45–44} whereas random copolymers exhibiting decreased crystallinity and enhanced flexibility could serve as a better choice of soft midblock.\textsuperscript{45–47} By replacing BnOH with BDM and through sequential monomer addition method, a series of ABA-type triblock polyester TPEs composed of random PCVL soft midblock (mass ratio of ε-CL:δ-VL = 1:1 is fixed for all TPEs synthesis) and PLLA hard end block were synthesized through sequential addition of monomer method at RT in the one-pot process (Figure 1b). GPC traces clearly showed the gradual shift to a higher molecular weight region with an increase in the contents of either the soft segment or hard segment (see Supporting Information Figure S3). \textsuperscript{1}H NMR spectra confirmed that the integral ratios of soft PCVL segment to PLLA hard segments were consistent with the monomer feed ratio and \textsuperscript{13}C NMR spectra revealed no observation of transesterification between PLLA and PCVL (see Supporting Information Figures S7–S24 and Table S3).

Microphase separation

Compared with TPE1 or TPE2 composed of PCL or PVL soft segments (see Supporting Information Figure S29), TPE3 to TPE9 exhibited a lower \( T_m \) value in the range of 24.7–29.2 °C attributed to soft segment PCVL and a \( T_m \) between 150.9 and 160.6 °C attributed to hard segment PLLA (see Supporting Information Figure S30–S32), thus, confirming the microphase separation of PCVL soft midblock and PLLA hard end block. Furthermore, SAXS was employed to study the morphology and effects of midblock composition on the microphase separation of the bulk triblock TPEs at RT. As a result, all of them exhibited the principal peaks indicative of microphase separation (Figures 2a and 2b), and the correlation lengths of the domains (\( d = 2\pi q^* \)) calculated from SAXS data are in the range of 27.3–52.3 nm (see Supporting Information Table S2). Further, as the soft segment contents increased, the primary scattering peaks gradually shifted toward the low \( q \) side, indicating the enlargement of microphase-separated domains. Moreover, AFM results also clearly demonstrated the microphase separation of TPE8 with high PLLA contents, consistent with the results obtained by the SAXS test (see Supporting Information Figures S44 and S45). These results clearly demonstrated the immiscibility of soft midblock PCVL and hard end block PLLA due to their differences in the polarity and crystallinity, indicating that all these TPEs are composed of a well-defined interpenetrated network of hard crystal skeleton and entangled soft “amorphous” network.

Mechanical properties of TPEs

To measure mechanical properties, TPE films were prepared from these triblock copolymers by a solvent-casting method. They were colorless and highly transparent without air bubbles. Uniaxial tensile testing showed that TPE1 or TPE2 with either PCL or PVL as soft segment exhibited comparable ultimate tensile strength (35.5 vs 35.4 MPa) and different elongation at break (1200% vs 953%). However, both showed clear yield points, followed by a cold drawing, indicating plastic deformation at a low elongation of 8–20% (see Supporting Information Figure S34).\textsuperscript{48} Although TPE3 with PCVL soft midblock showed weaker tensile strength (13.6 MPa), the elongation at break was significantly enhanced to 1552%, and no yield stress and cold stretching were observed (Figure 3), thus, confirming that PCVL is a better candidate for the soft segment in TPEs syntheses than PCL or PVL. By fixing the length of hard segments, increasing the ε-CL/δ-VL molar ratio from 200:228 to 300:342 and 400:456 led to the production of TPEs with high elongation at break from 1552% to 2000% and 2100% and strong tensile strength from 13.6 MPa to 33.8 MPa and 46.3 MPa, hence, exhibiting increased toughness from 109 MJ/m\(^3\) to 296 MJ/m\(^3\) and 445 MJ/m\(^3\), respectively (Figure 3). To the best of our knowledge, TPE5 with the longest soft segment (ε-CL:δ-VL = 400:456) represented supertough aliphatic polyester TPEs with the highest toughness value of 445 MJ/m\(^3\) so far. This phenomenon, in particular, attracted our attention since it contradicted a previous study that

![Figure 2] SAXS profiles of (a) 1D curves and (b) 2D curves for TPE3-TPE5 obtained at RT.
Moreover, we investigated the and Figure ±25 30 58.6 ±25 2.2 296 49 ± at fi ± b 41 65.9 73 2.1 334 400:456) but The numbers represent the monomer feed ratio to the initiator. 25 50 size TPE 28 13.6 25 50 These 28 13.6 25 1.5 409 1.5 109 1.6 109 Absolute molecular weight (µg/mol) 1.5 44 56.4 ± 75 1.5 289 ɛ 23 87 53.1 50 46.3 MPa to 56.4 MPa and 71.5 MPa, whereas the elongation at break decreased from 2100% to 1678% and 1365%, respectively (runs 5 vs 6 and 7, Table 1 and Figure 3). A similar trend was observed for TPEs with a fixed 300:342 r-CL:8-VL molar ratio, consistent with previous literatures.22,25,26 We observed that the higher the hard domain contents, the harder the crystal skeleton (or physical cross-linking points), thus, enhancing the tensile strength of TPEs, but sacrificed elongation at break.49 These results revealed that PCVL soft midblock played an essentially important role in affecting the toughness of the TPEs (vide infra).

Stereocomplex formed between two opposite chiral polymers exhibited improved mechanical properties and thermal properties compared with their parent polymers. Therefore, it could be utilized to modify the thermal resistance and long-lasting durability of the polymers effectively.50-52 By simply mixing 25PDLA-300/342PCVL-25PDLA with 25PLLA,300/342PCVL-25PLLA together, stereocomplex 25PDLLA-300/342PCVL-25PDLA was prepared, which exhibited significantly enhanced tensile strength (53.1 MPa), high stretchability (1722%), and superior toughness of 409 MJ/m2, hence, highlighting the significant impact of stereocomplexation on the improvement of TPEs’ mechanical properties (run 10, Table 1, see Supporting Information Figure S35). Compared with engineering stress-strain curves, the actual stress-strain curves were also indispensable for evaluating the mechanical performance of materials. As shown in Supporting Information Figure S36, TPE7 exhibited the most robust true tensile strength up to 1000 MPa, comparable with special engineering plastics.53,54 Surprisingly, a 0.996 g of TPE7 sample with 0.45 mm thickness could lift a 30 kg water tank successfully (see Supporting Information Movie S1), which is over 30,000 times heavier than itself. Moreover, 50 g of TPE5 could be synthesized from a high multigram-scale polymerization in a one-pot process and employed to prepare a 32 × 39 cm2 size TPE film (see Supporting Information Figure S43). Collectively, these results demonstrated the practicability of this method.

![Figure 3 | The stress–strain curves of different TPEs.](image)

showed that elongation at break and tensile strength were mutually exclusive. Moreover, we investigated the impact of hard block contents on the mechanical properties of TPEs. It turned out that for TPE5 to TPE7 with the same soft block contents (r-CL:8-VL = 400:456) but varying hard end block contents from 25 to 50 and 75, the ultimate tensile strength values increased from 46.3 MPa to 56.4 MPa and 71.5 MPa, whereas the elongation at break decreased from 2100% to 1678% and 1365%, respectively (runs 5 vs 6 and 7, Table 1 and Figure 3). A similar trend was observed for TPEs with a fixed 300:342 r-CL:8-VL molar ratio, consistent with previous literatures.22,25,26 We observed that the higher the hard domain contents, the harder the crystal skeleton (or physical cross-linking points), thus, enhancing the tensile strength of TPEs, but sacrificed elongation at break.49 These results revealed that PCVL soft midblock played an essentially important role in affecting the toughness of the TPEs (vide infra).

Stereocomplex formed between two opposite chiral polymers exhibited improved mechanical properties and thermal properties compared with their parent polymers. Therefore, it could be utilized to modify the thermal resistance and long-lasting durability of the polymers effectively.50-52 By simply mixing 25PDLA-300/342PCVL-25PDLA with 25PLLA,300/342PCVL-25PLLA together, stereocomplex 25PDLLA-300/342PCVL-25PDLA was prepared, which exhibited significantly enhanced tensile strength (53.1 MPa), high stretchability (1722%), and superior toughness of 409 MJ/m2, hence, highlighting the significant impact of stereocomplexation on the improvement of TPEs’ mechanical properties (run 10, Table 1, see Supporting Information Figure S35). Compared with engineering stress-strain curves, the actual stress-strain curves were also indispensable for evaluating the mechanical performance of materials. As shown in Supporting Information Figure S36, TPE7 exhibited the most robust true tensile strength up to 1000 MPa, comparable with special engineering plastics.53,54 Surprisingly, a 0.996 g of TPE7 sample with 0.45 mm thickness could lift a 30 kg water tank successfully (see Supporting Information Movie S1), which is over 30,000 times heavier than itself. Moreover, 50 g of TPE5 could be synthesized from a high multigram-scale polymerization in a one-pot process and employed to prepare a 32 × 39 cm2 size TPE film (see Supporting Information Figure S43). Collectively, these results demonstrated the practicability of this method.

Table 1 | Summary of Ultimate Tensile Properties of the Renewable Aliphatic Polyester TPEs

| Run | Sample Name | Sample | Mw (kg/mol) | D | εb (%) | σb (MPa) | Toughness (MJ/m²) |
|-----|-------------|--------|-------------|---|--------|-----------|------------------|
| 1   | TPE1        | 25PDLA-400/342PCL-25PLLA | 41.6 | 1.08 | 1200 ± 140 | 35.4 ± 3.3 | 252 ± 53 |
| 2   | TPE2        | 25PLLA,456PVL-25PLLA | 41.1 | 1.18 | 953 ± 150 | 35.5 ± 3.2 | 188 ± 73 |
| 3   | TPE3        | 25PDLA-200/250PCVL-25PLLA | 47.4 | 1.04 | 1552 ± 28 | 13.6 ± 1.6 | 109 ± 36 |
| 4   | TPE4        | 25PDLA-300/342PCVL-25PLLA | 67.2 | 1.08 | 2000 ± 80 | 33.8 ± 2.2 | 296 ± 18 |
| 5   | TPE5        | 25PDLA-400/456PCVL-25PLLA | 79.2 | 1.09 | 2100 ± 65 | 46.3 ± 1.4 | 445 ± 12 |
| 6   | TPE6        | 50PDLA-400/456PCVL-50PLLA | 87.0 | 1.07 | 1678 ± 44 | 56.4 ± 3.4 | 394 ± 23 |
| 7   | TPE7        | 75PDLA-400/456PCVL-75PLLA | 96.1 | 1.06 | 1365 ± 107 | 71.5 ± 2.1 | 334 ± 13 |
| 8   | TPE8        | 50PDLA-300/342PCVL-50PLLA | 74.3 | 1.09 | 1446 ± 30 | 58.6 ± 12 | 335 ± 52 |
| 9   | TPE9        | 75PDLA-300/342PCVL-75PLLA | 78.7 | 1.09 | 1290 ± 41 | 65.9 ± 15 | 289 ± 18 |
| 10  | TPE10       | 25PDLLA-300/342PCVL-25PDLLA | / | / | 1722 ± 87 | 53.1 ± 1.5 | 409 ± 12 |

* TPE samples were produced from polymerization performed in mixed solvents of toluene (TOL) and CH₂Cl₂ at ambient temperature (~25 °C) with [r-CL]₀ = 0.50 M, [s-VL]₀ = 0.57 M, [LLA] = 0.25 M in CH₂Cl₂.

a The numbers represent the monomer feed ratio to the initiator.

b Absolute molecular weight (Mw) and D determined by GPC using a LS detector.
c εb, elongation at break; σb, tensile strength. Average values and standard deviations were obtained from the tensile test of three samples with an extension rate of 15 mm-min⁻¹. Toughness was calculated as the area under the stress-strain curve according to eq 1.

DOI: 10.31635/ccschem.021.202100897

CCS Chem. 2021, 3, 1522–1531
Toughening mechanism

To dig into the toughening mechanism, we utilized the Gaussian model of Haward and Thackray to investigate the tensile deformation behavior of these produced TPE networks, using true stress $\sigma$ as a function of $(\lambda^{2-1}/\lambda)$ ($\lambda = l/l_0$, see Supporting Information Figure S37).\(^{55-57}\) The corresponding elastic network modulus (G) could be obtained from the slope of the curves (where $\lambda^{2-1}/\lambda > 100$, see Supporting Information Table S4) and revealed that the modulus was enhanced with the hard segment contents and the highest modulus was only 7.30 MPa. Therefore, we inferred that these TPEs possessed a very flexible elastic network, probably due to the lower degree of crystallinity of PCVL resulting from the copolymerization of ε-CL and δ-VL and the incorporation of PLLA end blocks. This led to a soft segment with $T_m$ close to RT and elastic networks with low crystallinity that were perfectly entangled “amorphous” networks under such conditions. These results well explained why high stretchability could be achieved by our strategy but still did not address the problem of how the tensile strength was also enhanced at the same time.

As shown in Supporting Information Figure S37, we observed two linear dependencies at different strain regimes, indicating these TPE samples exhibited tensile deformation behavior of two Gaussian networks of different moduli. Taking TPE7 (see Supporting Information Figure S37b) as an example, the hardening point (H-point) could be determined by the cross point of two tangent lines derived from two networks.\(^{55}\) Based on the slope of two tangent lines, we presumed the second Gaussian network had a higher modulus than the first one. It is known that the occurrence of H-point indicated the strain-hardening and change of network modulus during stretching, probably attributable to the presence of strain-induced crystallization (SIC).\(^{49,55}\) To verify it, we performed in situ WAXD measurement to investigate the possible crystallization behavior of TPE3 to TPE5 with different soft block contents during stretching at RT. Prior to stretching, the initial crystallinity value of TPE3 was only 0.05 (Figure 4a). During stretching, we observed the diffraction patterns of oriented crystallization (see Supporting Information Figure S38). Quantitative analysis showed its crystallinity kept increasing with a continuous straining sample bar until 0.12 was reached for stretching of 650% (Figure 4f), indicating the existence of the SIC effect during stretching. As control experiments, the strain behaviors of TPE1 and TPE2 composed of either PCL or PVL soft midblock, studied by WAXD (Figures 4d and 4e). Note that both samples exhibited high crystallinity before stretching, which might be attributed to the semicrystalline nature of PCL or PVL. Although we still observed the oriented crystallization during stretching (see Supporting Information Figures S41 and S42), the total crystallinity of both samples kept decreasing, indicating that the original crystallinity was destroyed during stretching, thereby well explaining the presence of yield point in both TPEs (Figure 4f). Besides, with an increase in soft segment contents, both TPE4 and TPE5 exhibited higher crystallinity before and after stretching in comparison with TPE3 (Figures 4b, 4c, and 4f also see Supporting Information Figures S39 and S40), which indicated that not only molecular weight but also the microstructure of soft segment of TPEs were closely related to the SIC effect (vide infra). Altogether, these results undoubtedly, demonstrated that the dynamic soft segment PCVL not only provided a flexible elastic network to afford large elongation TPEs but also played a significant role in affecting the SIC effect, accounting for the simultaneous improvement in both tensile strength and elongation at break, achieved by our Mg(II)/BDM system. Then another question arose: What critical parameter contributes to the SIC effect found in these triblock polyester-based TPEs? Pan et al.\(^{23}\) has already reported the employment of PCVL as a soft segment and PLA as a hard segment system for TPEs syntheses with the catalysis of Sn(Oct)_2 and 1,6-hexanediol system. However, the generated TPEs’ elongation at break was less than 900%, with a tensile strength not more than 8.0 MPa.

To find the answer to the above question, we monitored the polymer composition changing with the reaction time by both Sn(Oct)_2/BDM and Mg(II)/BDM catalyst system, respectively. It turned out that the polymerization rate of δ-VL is similar to that of ε-CL for Sn(Oct)_2/BDM and Mg(II)/BDM system, respectively. It turned out that the polymerization rate of δ-VL is similar to that of ε-CL for Sn(Oct)_2/BDM.\(^{13}\) C NMR spectra revealed that the produced PCVL was a more random copolymer because we observed an equal ratio of the homo-(CL-CL and VL-VL) and hetero-(CL-VL and VL-CL) dyad sequences [VL-CL (0.25), CL-CL (0.26), VL-VL (0.25), and CL-VL (0.24)] and the polymer composition remained nearly unchanged throughout the polymerization (see Supporting Information Figure S27). In sharp contrast, the polymerization rate of δ-VL is about 4.0 times faster than that of ε-CL for Mg(II)/BDM. As shown in Figure 5, the monomer conversion reached 40% and 15% for δ-VL and ε-CL within 3.5 min, with integrals of 0.55 and 0.08 for VL-VL and CL-CL linkages respectively, indicating that the PVL was generated predominately at the beginning of polymerization. The polymerization rate of δ-VL slowed down with its rapid consumption. The integrals of CL-VL, VL-CL, and CL-CL linkages, increased gradually, indicating that the random PCVL was formed as the majority at this stage. After δ-VL conversion reaching 95%, the integral of CL-CL increased rapidly, suggesting that the PCL was mainly generated in the late stage of the polymerization process. In combination with the fact that a diol was utilized as an
initiator, we inferred that the composition of the polymer gradually transited from the PVL center to both sides of the random-sequenced PCVL, followed by PCL capped at both ends of the polymer chain, thereby furnishing a block-like, gradient copolymer, PCL-PCVL-PCVL-PCL, exhibiting four unequal integrals of homo- and hetero-dyad sequences [VL-CL (0.20), CL-CL (0.26), VL-VL (0.34), and CL-VL (0.20)]. Such gradient structure was also confirmed by DSC analysis. Different from the PCVL obtained by Sn(Oct)$_2$ and 1,6-hexanediol only exhibiting one $T_m$ at 23.4 °C, the PCVL produced by Mg(II)/BDM showed two $T_m$ at 31.5 and 43.0 °C, attributed to the hetero-dyad sequence for PCVL and homo-dyad sequences for either PCL or PVL, respectively (see Supporting Information Figure S33). The peak at 43.5 °C disappeared after the copolymerization of PCVL with PLLA, indicating the reduced crystallinity of midblock PCVL resulting from incorporating PLLA into polymers. The reduction of crystallinity was beneficial for stretching. Upon stretching, PCL or PVL in the entangled soft blocks were elongated and arranged orderly manner, leading to the oriented crystallization, which generated a new hard skeleton filling into the elastic network as physical cross-linking points enhancing the tensile strength of TPEs. That is to say, the block-like gradient microstructure of PCVL was the key to the preparation of TPEs with simultaneous improvements of both elongation at break and tensile strength. We stretched a sample and tied a knot to maintain the stretching, then characterized its thermal properties by DSC analysis to verify our assumption. The observance of $T_m$ peak at 39.0 °C again clearly demonstrated the occurrence of strain-induced recrystallization during stretching (see Supporting Information Figure S32).

**Figure 4** (a–f) Quantitative analysis of WAXD for TPEs with different soft segment contents.
Conclusion

We developed an Mg(II)/alcohol system to catalyze living/controlled ROP of cyclic lactones at RT. Owing to its living/controlled nature, a series of triblock polyester TPEs were prepared successfully through sequential addition of monomers in a one-pot manner, using PLLA as a hard segment and random copolymer PCVL as the soft segment. The control over TPEs’ molecular weight and composition could be realized by simple adjustment of the monomers feed ratio. With fixed soft segments, increasing the hard segment contents enhanced the tensile strength significantly (up to 71.5 MPa) but decreased the stretchability. Interestingly, with fixed hard segments, both elongation at break and tensile strength of the TPEs were enhanced simultaneously, with increasing soft segment contents, thus, achieving a supertough polyester TPE with high stretchability (2100%), strong tensile strength (46.3 MPa), and the world’s highest record of toughness (445 MJ/m$^3$). Furthermore, monitoring of polymer composition with reaction time revealed that Mg(II)/BDM system produced a block-like, gradient PCL-PCVL-PVL-PCVL-PCL copolymer. Systematic investigations, coupled with control experiments, showed that such block-like, gradient copolymer as soft midblock is crucial for the toughening of TPEs, which provided a flexible elastic network to improve the ductility, and led to SIC, thereby enhancing the tensile strength at the same time. To the best of our knowledge, this is the first time of employing a highly efficient and selective catalyst system without the requirement of a specific functionalized group to enable the synthesis of sustainable, supertough polyester TPEs. The fabricated TPEs had both high stretchability and strong tensile strength from the ROP of traditional cyclic lactones, achieved by simply adjusting the composition and microstructure of polymers. The investigation toward the application of these supertough TPEs in the related fields is underway.

Supporting Information

Supporting Information is available and includes experimental details, GPC data, NMR spectra, DSC spectra, WAXD spectra, and stress–strain curves.

Conflict of Interests

The authors declare no competing interests.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (grant no. 22071077) and Open Research Fund of State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (grant no. 2019-16) to Y.Z., (grant no. 51525305) to Y.M., and (grant no. 51988102) to X.C.

References

1. Wang, W.; Lu, W.; Goodwin, A.; Wang, H.; Yin, P.; Kang, N.-G.; Hong, K.; Mays, J. W. Recent Advances in Thermoplastic Elastomers from Living Polymerizations: Macromolecular Architectures and Supramolecular Chemistry. Prog. Polym. Sci. 2019, 95, 1–31.
2. Ye, H.; Zhang, K.; Kai, D.; Li, Z.; Loh, X. J. Polyester Elastomers for Soft Tissue Engineering. Chem. Soc. Rev. 2018, 47, 4545–4580.
3. Chen, Q.; Liang, S.; Thouas, G. A. Elastomeric Biomaterials for Tissue Engineering. Prog. Polym. Sci. 2013, 38, 584–671.
4. The Future of High-Performance Elastomers to 2024; Smithers Rapra, 2019.
5. Chen, Y.; Kushner, A. M.; Williams, G. A.; Guan, Z. Multi-phase Design of Autonomic Self-Healing Thermoplastic Elastomers. Nat. Chem. 2012, 4, 467–472.
6. Hillmyer, M. A.; Tolman, W. B. Aliphatic Polyester Block Polymers: Renewable, Degradable, and Sustainable. Acc. Chem. Res. 2014, 47, 2390–2396.
7. Creton, C. 50th Anniversary Perspective: Networks and Gels: Soft but Dynamic and Tough. Macromolecules 2017, 50, 8297–8316.
8. Ritchie, R. O. The Conflicts between Strength and Toughness. Nat. Mater. 2011, 10, 817–822.
9. Cui, W.; King, D. R.; Huang, Y.; Chen, L.; Sun, T. L.; Guo, Y.; Saruwatari, Y.; Hui, C. Y.; Kurokawa, T.; Gong, J. P. Fiber-Reinforced Viscoelastomers Show Extraordinary...
Crack Resistance That Exceeds Metals. Adv. Mater. 2020, 32, 1907180.
10. Guo, D.; Goh, Y. L. Y.; Shweta, A.; Wai, Y. Y. Recent Progress in Additive Manufacturing of Fiber Reinforced Polymer Composite. Adv. Mater. Technol. 2019, 4, 1800271.
11. Matsuda, T.; Nakajima, T.; Gong, J. P. Fabrication of Tough and Stretchable Hybrid Double-Network Elastomers Using Ionic Dissociation of Polyelectrolyte in Nonaqueous Media. Chem. Mater. 2019, 31, 3766–3776.
12. Rao, Y.-L.; Chortos, A.; Pfatter, R.; Lissel, F.; Chiu, Y.-C.; Feig, V.; Xu, J.; Kurosawa, T.; Gu, X.; Wang, C.; He, M.; Chung, J. W.; Bao, Z. Stretchable Self-Healing Polymeric Dielectrics Cross-Linked through Metal–Ligand Coordination. J. Am. Chem. Soc. 2016, 138, 6020–6027.
13. Wang, X.; Zhan, S.; Lu, Z.; Li, J.; Yang, Y.; Qiao, Y.; Men, Y.; Sun, J. Healable, Recyclable, and Mechanically Tough Polyurethane Elastomers with Exceptional Damage Tolerance. Adv. Mater. 2020, 32, 2005759.
14. Gu, L.; Jiang, Y.; Hu. J. Bioinspired Spurylevinyl alcohol)-Silk Hybrids: Two-Way Water-Sensitive Shape-Memory Materials, Mater. Today Commun. 2018, 17, 419–426.
15. Song, Y.; Liu, Y.; Qi, T.; Li, G. L. Towards Dynamic but Supertough Healable Polymers through Biomimetic Hierarchical Hydrogen-Bonding Interactions. Angew. Chem. Int. Ed. 2018, 57, 13838–13842.
16. Gu, L.; Jiang, Y.; Hu. J. Scalable Spider-Silk-like Super-tough Fibers Using a Peptide Protein Polymer. Adv. Mater. 2019, 31, 1904371.
17. Schneiderman, D. K.; Hillmyer, M. A. 50th Anniversary Perspective: There Is a Great Future in Sustainable Polymers. Macromolecules 2017, 50, 3733–3749.
18. Zhu, Y.; Romain, C.; Williams, C. K. Sustainable Polymers from Renewable Resources. Nature 2016, 540, 354–362.
19. Gregory, G. L.; Sulley, G. S.; Carrodegues, L. P.; Chen, T. T. D.; Santamart, A.; Terrill, N. J.; Lee, K.-Y.; Williams, C. K. Triblock Polymer Thermoplastic Elastomers with Semi-Aromatic Polymer End Blocks by Ring-Opening Copolymerization. Chem. Sci. 2020, 11, 6567–6581.
20. Fang, C.; Wang, X.; Chen, X.; Wang, Z. Mild Synthesis of Environment-Friendly Thermoplastic Triblock Copolymer Elastomers through Combination of Ring-Opening and RAFT Polymerization. Polym. Chem. 2019, 10, 3610–3620.
21. Zhu, Y.; Radlauer, M. R.; Schneiderman, D. K.; Shaffer, M. S. P.; Hillmyer, M. A.; Williams, C. K. Multiblock Polymers Demonstrating High Elasticity and Shape Memory Effect. Macromolecules 2018, 51, 2466–2475.
22. Watts, A.; Kurokawa, N.; Hillmyer, M. A. Strong, Resilient, and Sustainable Aliphatic Polyester Thermoplastic Elastomers. Biomacromolecules 2017, 18, 1845–1854.
23. Huang, Y.; Chang, R.; Han, L.; Shan, G.; Bao, Y.; Pan, P. ABA-Type Thermoplastic Elastomers Composed of Poly(ε-caprolactone-co-σ-valerolactone) Soft Midblock and Poly-morphic (lactic acid) Hard End blocks. ACS Sustain. Chem. Eng. 2016, 4, 121–128.
24. Schneiderman, D. K.; Hillmyer, M. A. Aliphatic Polyester Block Polymer Design. Macromolecules 2016, 49, 2419–2428.
25. Schneiderman, D. K.; Hill, E. M.; Martello, M. T.; Hillmyer, M. A. Poly(lactide)-Block-Poly(l-caprolactone-co-ε-decalactone)-Block-Poly(lactide) Copolymer Elastomers. Polym. Chem. 2015, 6, 3641–3651.
26. Martello, M. T.; Schneiderman, D. K.; Hillmyer, M. A. Synthesis and Melt Processing of Sustainable Poly(ε-decalactone)-block-Poly(lactide) Multiblock Thermoplastic Elastomers. ACS Sustain. Chem. Eng. 2014, 2, 2519–2526.
27. Xiong, M.; Schneiderman, D. K.; Bates, F. S.; Hillmyer, M. A.; Zhang, K. Scalable Production of Mechanically Tunable Block Polymers from Sugar. PNAS 2014, 111, 8357–8362.
28. Shin, J.; Lee, Y.; Tolman, W. B.; Hillmyer, M. A. Thermoplastic Elastomers Derived from Menthode and Tulipalin A. Biomacromolecules 2012, 13, 3833–3840.
29. Martello, M. T.; Hillmyer, M. A. Poly(lactide-Poly(6-methy-1-caprolactone)-Polylactide Thermoplastic Elastomers. Macromolecules 2011, 44, 8537–8545.
30. Frick, E. M.; Zalkusky, A. S.; Hillmyer, M. A. Characterization of Poly(lactide-b-polyisoprene-b-poly(lactide) Thermoplastic Elastomers. Biomacromolecules 2003, 4, 216–223.
31. Wanamaker, C. L.; Bluemle, M. J.; Pitet, L. M.; O’Leary, L. E.; Tolman, W. B.; Hillmyer, M. A. Consequences of Polylactide Stereochemistry on the Properties of Poly(lactide-Polymenthide-Poly(lactide) Thermoplastic Elastomers. Biomacromolecules 2009, 10, 2904–2911.
32. Watts, A.; Hillmyer, M. A. Aliphatic Polyester Thermoplastic Elastomers Containing Hydrogen-Bonding Ureido-pyrimidinone Endgroups. Biomacromolecules 2019, 20, 2598–2609.
33. De Hoe, G. X.; Zumstein, M. T.; Tiegs, B. J.; Brutman, J. P.; McNell, K.; Sander, M.; Coates, G. W.; Hillmyer, M. A. Sustainable Polyester Elastomers from Lactones: Synthesis, Properties, and Enzymatic Hydrolyzability. J. Am. Chem. Soc. 2018, 140, 963–973.
34. Brutman, J. P.; Hoe, G. X. D.; Schneiderman, D. K.; Le, T. N.; Hillmyer, M. A. Renewable, Degradable, and Chemically Recyclable Cross-Linked Elastomers. Ind. Eng. Chem. Res 2016, 55, 11097–11106.
35. Cohn, D.; Salomon, A. H. Designing Biodegradable Multiblock PCL/PLA Thermoplastic Elastomers. Biomaterials 2005, 26, 2297–305.
36. Zhang, J.; Xu, J.; Wang, H.; Jin, W.; Li, J. Synthesis of Multiblock Thermoplastic Elastomers Based on Biodegradable Poly(lactic acid) and Polycaprolactone. Mater. Sci. Eng. C 2009, 29, 889–893.
37. Hammersley, A. P.; Brown, K.; Burmeister, W.; Claustre, L.; Gonzalez, A.; Mcsweeney, S.; Mitchell, E.; Moy, J. P.; Svensson, S. O.; Thompson, A. W. Calibration and Application of an X-ray Image Intensifier/Charge-Coupled Device Detector for Monochromatic Macromolecular Crystallography. J. Synchrotron Radiat. 1997, 4, 67–77.
38. Liu, W.; Fang, C.; Wang, S.; Huang, J.; Qiu, X. High-Performance Lignin-Containing Polyurethane Elastomers with Dynamic Covalent Polymer Networks. Macromolecules 2019, 52, 6474–6484.
39. Wan, Y.; Bai, Y.; Xu, H.; He, J.; Zhang, Y. Highly Iososelective Ring-Opening Polymerization of rac-Lactide Using Chiral Binuclear Aluminum Catalyst. Macromol. Rapid. Commun. 2020, 42, 2000491.

DOI: 10.31635/ccschem.021.202100897
CCS Chem. 2021, 3, 1522–1531
40. Zhao, W.; Wang, Q.; Cui, Y.; He, J.; Zhang, Y. Living/Controlled Ring-Opening (Co)polymerization of Lactones by Al-Based Catalysts with Different Sidearms. Dalton Trans. 2019, 48, 7167-7178.
41. Wang, Q.; Zhao, W.; He, J.; Zhang, Y.; Chen, E. Y. Living Ring-Opening Polymerization of Lactones by N-Heterocyclic Olefin/Al(C6F5)3 Lewis Pairs: Structures of Intermediates, Kinetics, and Mechanism. Macromolecules 2017, 50, 123-136.
42. Zhang, X.; Fevre, M.; Jones, G. O.; Waymouth, R. M. Catalysis as an Enabling Science for Sustainable Polymers. Chem. Rev. 2018, 118, 839-885.
43. Armentano, I.; Bitinis, N.; Fortunati, E.; Mattioli, S.; Rescignano, N.; Verdejo, R.; Lopez-Manchado, M. A.; Kenny, J. M. Multifunctional Nanostructured PLA Materials for Packaging and Tissue Engineering. Prog. Polym. Sci. 2013, 38, 1720-1747.
44. Jamshidian, M.; Tehrany, E. A.; Imran, M.; Jacquot, M.; Desobry, S. Poly-Lactic Acid: Production, Applications, Nanocomposites, and Release Studies. Compr. Rev. Food. Sci. F. 2010, 9, 552-571.
45. Makiguchi, K.; Satoh, T.; Kakuchi, T. Diphenyl Phosphate as an Efficient Cationic Organocatalyst for Controlled/Living Ring-Opening Polymerization of δ-Valerolactone and ε-Caprolactone. Macromolecules 2011, 44, 1999-2005.
46. Pan, P.; Inoue, Y. Polymorphism and Isomorphism in Biodegradable Polyesters. Prog. Polym. Sci. 2009, 34, 605-640.
47. Faÿ, F.; Renard, E.; Langlois, V.; Linossier, I.; Vallée-Rehel, K. Development of Poly(ε-caprolactone-co-L-lactide) and Poly(ε-caprolactone-co-δ-valerolactone) as New Degradable Binder Used for Antifouling Paint. Eur. Polym. J. 2007, 43, 4800-4813.
48. Jeon, O.; Lee, S.-H.; Kim, S. H.; Lee, Y. M.; Kim, Y. H. Synthesis and Characterization of Poly(L-lactide)-Poly(ε-caprolactone) Multiblock Copolymers. Macromolecules 2003, 36, 5585-5592.
49. Yang, X.; Sun, Y.; Liao, T.; Men, Y. Strain Dependent Evolution of Structure and Stress in Propylene-Based Elastomer During Stress Relaxation. Polymer 2020, 201, 122612.
50. Worch, J. C.; Prydderch, H.; Jimaja, S.; Bexis, P.; Becker, M. L.; Dove, A. P. Stereocchemical Enhancement of Polymer Properties. Nat. Rev. Chem. 2019, 3, 514-535.
51. Bertin, A. Emergence of Polymer Stereocomplexes for Biomedical Applications. Macromol. Chem. Phys. 2012, 213, 2329-2352.
52. Tsuji, H. Poly(lactic acid) Stereocomplexes: A Decade of Progress. Adv. Drug. Deliv. Rev. 2016, 107, 97-135.
53. Diez-Pascual, A. M.; Diez-Vicente, A. L. Nano-TiO2 Reinforced PEEK/PEI Blends as Biomaterials for Load-Bearing Implant Applications. ACS Appl. Mater. Interfaces. 2015, 7, 5561-5573.
54. Lu, X.; Luo, Y.; Li, Y.; Bao, C.; Wang, X.; An, N.; Wang, G.; Sun, J. Polymeric Complex Nanoparticles Enable the Fabrication of Mechanically Superstrong and Recyclable Poly(aryl ether sulfone)-based Polymer Composites. CCS Chem. 2020, 2, 524-532.
55. Miao, Z.; Men, Y. Temperature Dependent Network Properties of Amorphous PCT during Tensile Stretching. Polymer 2020, 186, 120358.
56. Haward, R. Strain Hardening of Thermoplastics. Macromolecules 1993, 26, 5860-5869.
57. Men, Y.; Rieger, J.; Strobl, G. Role of the Entangled Amorphous Network in Tensile Deformation of Semicrystalline Polymers. Phys. Rev. Lett. 2003, 91, 095502.