Block Copolymer Materials from the Organocatalytic Ring-Opening Polymerization of a Pentaerythritol-Derived Cyclic Carbonate

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ABSTRACT: 9-Phenyl-2,4,8,10-tetraoxaspiro[5,5]undecanone (PTO) was synthesized from pentaerythritol via the acid-catalyzed acetal formation reaction with benzaldehyde and subsequent ring closure with ethyl chloroformate. The cyclic carbonate monomer was subsequently polymerized by ring-opening polymerization (ROP) initiated from 1,4-butanediol (1,4-BDO) using the 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea and 1,8-diazabicyclo[5.4.0]undec-7-ene dual organocatalytic system. It was found that the organocatalyst allowed for the synthesis of well-defined polymers with minimal adverse side reactions and low dispersities. This system was then employed in the ROP of PTO initiated from an α, ω -dihydroxy poly(caprolactone) (PCL) macroinitiator, with varying molecular weights, to yield a series of

A-B-A block copolymers. These materials were characterized by ¹H NMR spectroscopy, gel permeation chromatography, differential scanning calorimetry, thermogravimetric analysis and tensile analysis. It was found that the chain extension from PCL with poly(PTO) (PPTO) blocks yielded a thermoplastic material with superior tensile properties (elongation and Young's modulus) to that of the PCL homopolymer. Furthermore, it was noted that the addition of PPTO could be employed to alter the crystallization properties (crystallization temperature (T_c), and percentage crystallization) of the central PCL block. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 2279–2286

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INTRODUCTION As a result of their low toxicity, tunable biodegradability and biocompatibility, in conjunction with their versatile mechanical properties, both aliphatic poly(ester)s and poly(carbonate)s have been of recent interest in the field of renewable biomaterials.¹⁻⁴ As a consequence of these distinct advantages over conventional aliphatic hydrocarbonbased polymers, these materials are excellent candidates in the production of biodegradable thermoplastic elastomers (TPEs) for biomedical applications.⁵⁻⁹

The utilization of ring-opening polymerization (ROP) of cyclic ester/carbonate monomers to achieve precisely-defined polymers employing organocatalysts, such as diphenyl phosphate (DPP), 1,5,7-triazabicyclo[4.4.0]dec-5-ene or the dual-catalytic system of 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea (TU) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) have been extensively studied in recent years.^{10–14} As a consequence of their relatively low toxicity, mild reaction conditions, facile removal, and reduced propensity for adverse side reactions in comparison to traditional metal-based catalysts, organocatalysts have facilitated the advancement of ROP in the synthesis of well-defined poly(ester/carbonate)s for biomedical applications.^{15–19} Aliphatic poly(ester)s have

been extensively synthesized from the ROP of a vast range of readily available cyclic esters such as lactide, ε caprolactone (ε -CL), δ -valerolactone etc. Whilst this range of monomers allows for the modulation of physiochemical properties such as phase transition temperatures, toughness, stiffness and degradability, homopoly(ester)s have been shown to display relatively poor mechanical properties, that is, low percentage elongations, inelasticity, brittleness etc.^{20,21}

In more recent studies, the introduction of low $T_{\rm g}$ poly(carbonate)s, such as trimethylene carbonate, into poly(ester)based materials has been shown to yield biomaterials with improved mechanical properties and degradability, that is, higher degrees of flexibility, higher elongation/elasticity, tunable degradation profiles etc.^{22,23} These materials may be produced either by the copolymerization of cyclic(ester/ carbonate) monomers or through chain extension from homopolymer macro-initiators to yield block copolymer-type structures.²⁴⁻²⁶ The synthesis of cyclic carbonate monomers is therefore of great interest, as these compounds offer a facile route to the evolution of novel biomaterials with superior mechanical properties.²⁷⁻³⁰ Cyclic carbonates can be prepared

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by the ring-closure of diol precursors and as a consequence of the wide range of diol precursors available, a plethora of novel carbonate monomers with varied functionalities can be synthesized through the ring-closure of functional or modified diols.^{31–33} These functionalities can in turn be employed to dictate the physio-chemical properties of the resultant materials such as glass transition (T_g), crystallization/melting temperatures (T_c/T_m), tensile properties etc.^{34,35}

The premise for the utilization of an A-B-A system in the synthesis of TPEs is based on the concept of an amorphouscrystalline or "hard-soft" phase separated system.36-39 In these A-B-A systems the interior block comprises of a low T_{g} (<25 °C) amorphous polymer [e.g., poly(oxyethylene glycol), poly(siloxane), poly(hexamethylene adipate glycol) etc.], which are flexible at ambient temperatures. Low molecular weight PCL has also traditionally been applied as a degradable soft block in TPEs.^{5,40} The terminal blocks, in contrast, generally comprise of high $T_{\rm g}$ polymers which display a higher order of crystallinity and self-association [e.g., poly(α methylene- γ -butyroactone), poly(styrene) etc.]. In more recent times the incorporation of renewable materials into these TPE systems, as either a single component or as a complete composite, has been of great interest fields such as regenerative medicine^{6,39,41-44} however few studies have focused on degradable, high Tg poly(carbonate)-based hard blocks.45,46

In this study we report the organocatalyzed ROP of 9-phenyl-2,4,8,10-tetraoxaspiro[5, 5]undecanone (PTO), initiated from 1,4-butanediol and subsequently from a poly(caprolactone) (PCL) α, ω -dihydroxy macro-initiator to synthesise an A-B-A triblock copolymer as a novel method to improve the mechanical properties of PCL through the introduction of phase separation from a high T_{g} poly(carbonate) hard block. Subsequently we report the compilation of an A-B-A triblock copolymer library based on varying molecular weights of A and B blocks in order to assess the effect of molecular structures on the physio-chemical properties of the resultant materials. The thermal properties (i.e., $T_{\rm g}$, $T_{\rm c}$, $T_{\rm m}$, percentage crystallinity) and stability of the triblock copolymers were analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), whilst their mechanical properties [i.e., Young's modulus (E) and elongation at break] were obtained via tensiometric analysis. We postulated that, with the incorporation of poly(PTO) (PPTO) as the hard block of an A-B-A TPE-type system, the mechanical properties of PCL could be improved by retarding any crystallinity of the PCL homopolymer and in turn allowing for the microphase separation of the A-B-A system.

EXPERIMENTAL

Materials

Pentaerythritol 98% was purchased from Acros Chemicals. Amberlyst A21 free base resin, ethyl chloroformate, benzaldehyde, and DBU (subsequently dried over CaH_2) were purchased from Sigma Aldrich. Hydrochloric acid (HCl 37%), ethyl acetate, toluene, dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF) were purchased from Fisher Scientific. Deuterated chloroform (CDCl₃) was purchased from Apollo Scientific and dried over activated 3Å molecular sieves. TU was synthesized as previously reported and was solubilized in dry CH_2Cl_2 before being dried over CaH_2 before filtration and solvent removal via standard Schlenk techniques to yield dry TU.¹³ Diphenylphosphate was purchased from Apollo Scientific Ltd. and dried for 3 days over phosphorous pentoxide (P₂O₅) in a vacuum desiccator. All chemicals and solvents were used as received unless stated otherwise.

Instrumental Methods

¹H and ¹³C NMR spectra were obtained on a Bruker DPX-400 spectrometer (400 MHz) at 293 K. All chemical shifts were reported as δ in parts per million (ppm) and referenced to the residual solvent signal [CDCl₃: ¹H, δ = 7.26 ppm; ¹³C, $\delta = 77.16$ ppm; (CD₃)SO: ¹H, $\delta = 2.50$ ppm; ¹³C, δ = 39.52]. Gel permeation chromatography (GPC) was used to determine the dispersities (D_M) and molecular weights of synthesized polymers. GPC was conducted in dimethylformamide (DMF) or chloroform (CHCl₃) using an Varian PL-GPC 50 system equipped with 2 \times PLgel 5 μ M MIXED-D columns in series and a differential refractive index (RI) detector at a flow rate of 1.0 mL min⁻¹. The systems were calibrated against Varian Polymer Laboratories Easi-Vial linear poly(methyl methacrylate) (PMMA) and poly(styrene) (PS) standards respectively and analyzed by the software package Cirrus v3.3. DSC and TGA were obtained using a Mettler Toledo DSC1 star and a TGA/DSC star system. DSC heating and cooling cycles were run in triplicate in series between -100and 150 °C under a nitrogen atmosphere at a heating rate of +/-10 °C min⁻¹ in a 40 μ L aluminum crucible. TGA was conducted between 20 and 300 °C at a heating rate of 10 °C min^{-1} in a 40 μ L aluminum crucible. Tensile data was obtained at ambient temperature by axially loading "dogbones" in a Tensiometric M100-1CT system with a load cell capacity of 1 kN and crosshead speed of 5 mm min⁻¹ with a premeasured grip-to-grip separation All values reported were obtained from an average of 10 repeat specimens and the results were recorded using winTest v4.3.2 software. Molten polymer samples were molded into "dog-bones" via compression moulding at 100 °C using a PTFE mold and allowed to cool to ambient temperature.

Synthesis and Ring Closure of Benzylidene Acetal Monoprotected Pentaerythritol

The benzylidene acetal-functionalized pentaerythritol-based diol was synthesized via the acid catalyzed acetal formation from benzaldehyde as previously reported in literature.⁴⁷⁻⁴⁹ In a clean round bottom flask, pentaerythritol (50 g, 36.7×10^{-2} mol) was suspended in 400 mL of deionized water and heated to 80 °C with stirring until all the solid had dissolved. The pentaerythritol solution was allowed to cool to ambient temperature before the addition of conc. HCl (1.5 mL, 14.8 mmol, HCl, 36 wt % in H₂O) with continual stirring for 15 min. Benzaldehyde (42.87 g, 40.4×10^{-2} mol) was added drop-wise to the acidified solution over 20 min and

allowed to stir for a further 2 h. The monofunctionalized product formed a white crystalline precipitate, which was collected by vacuum filtration before being purified by recrystallization from hot toluene to yield white crystals. Analysis was consistent with previous reports. (36.5 g, yield: 44%) ¹H NMR (400 MHz, *d*₆-DMSO) δ 7.47–7.29 (m, 1H), 5.40 (s, 1H), 4.59 (d, ²J_{H-H} = 29.8 Hz, 1H), 3.90 (d, ²J_{H-H} = 11.5 Hz, 1H), 3.79 (d, ²J_{H-H} = 11.5 Hz, 1H), 3.67 (s, 1H), 3.24 (s, 1H). ¹³C NMR (101 MHz, *d*₆-DMSO) δ 138.77 (s, C), 128.58 (s, 2 CH), 127.94 (s, 2 CH), 126.13 (s, CH), 100.65 (s, CH), 69.06 (s, 2 CH₂), 61.00 (s, CH₂), 59.52 (s, CH₂).

In a clean dry 2-necked round bottom flask, monobenzylidene-protected pentaerythritol (17 g, 76 mmol) was dissolved in 800 mL of THF and cooled to 0 °C using an icebath. Under an N₂ blanket, ethyl chloroformate (21.8 mL, 228 mmol) was slowly added to the diol solution and stirred for 30 min. Triethylamine (23.1 mL, 228 mmol) was added drop-wise to the cooled solution over a 45 min period and the reaction was allowed to stir for 3 h while being allowed to warm to ambient temperature. The resultant salt formed during the reaction was removed via vacuum filtration and was further rinsed with THF. The filtrate and washings were combined and solvent was removed in vacuo to yield offwhite crystals. The crude carbonate-monomer was purified by recrystallization from hot toluene to yield white crystals. The monomer was dissolved in dry CH₂Cl₂ and dried over activated 3 Å molecular sieves using standard Schlenk-line techniques. The solvent was removed under reduced pressure and the dry monomer stored in the glovebox. (9.88 g, yield: 52%). ¹H NMR (400 MHz, d_6 -DMSO) δ 7.48–7.35 (m, 5H), 5.55 (s, 1H), 4.65 (s, 2H), 4.18 (s, 2H), 3.92 (d, ${}^{2}J_{H-H} = 11.5$ Hz, 2H), 3.80 (d, ${}^{2}J_{H-H} = 11.5$ Hz, 2H). 13 C NMR (101 MHz, d_6 -DMSO) δ 147.63 (s, C=O), 137.81 (s, C), 129.00 (s, CH), 128.10 (s, CH), 126.21 (s, CH), 101.22 (s, CH), 70.61 (s, CH₂), 69.88 (s, CH₂), 68.25 (s, 2 CH₂).⁴⁷⁻⁴⁹

General Procedure for the Organocatalyzed ROP of PTO

All polymerizations were carried out using standard glovebox and Schlenk-line techniques. The ROP of PTO using 1 mol % DBU and 5 mol % TU was carried out in dry CDCl₃ at ambient temperature using 1,4-butanediol (1,4-BDO) as the initiator. In a clean dry vial, PTO (50 mg, 2 mmol) was dissolved in 500 μ L of CDCl₃ before the addition of freshly prepared stock solutions of DBU (30.4 μ L, 2 \times 10⁻² mmol, 0.1 mg μL^{-1} CDCl_3 stock), TU (740 μL , 1 \times 10 $^{-1}$ mmol, 50 mg mL⁻¹ CDCl₃ stock) and 1,4-BDO (29.5 μ L, 16 mmol, 0.1 mg μL^{-1} CDCl_3 stock). The polymerization was stopped by precipitation into hexanes and the polymer recovered via a silica plug. Silica plug conditions; the crude material was loaded onto the silica plug in CH₂Cl₂. The residual monomer and TU cocatalysts were eluted using CH_2Cl_2 ($R_f = 0.9$ and $R_{\rm f} = 0.8$, respectively) before a direct solvent switch to ethyl acetate was employed to elute the pure polymer ($R_{\rm f} = 0.9$), with the DBU catalyst remaining on the silica ($R_f = 0$). DP50 homopolymer; $^{1}\mathrm{H}$ NMR (250 MHz, CDCl_3) δ 7.58–7.30 (m, 250H), 5.43 (s, 50H), 4.57 (s, 100H), 4.24 - 3.79 (m, all other H), 3.25 (t, ${}^{2}J_{H-H} = 5.9$ Hz, 4H), 1.87–1.79 (m, 4H). $M_{W} = 11.7$ kg mol⁻¹, $\mathcal{D}_{M} = 1.12$ (RI detection, CHCl₃ GPC).

General Procedure for the Organocatalyzed ROP of ε-Caprolactone

All polymerizations were carried out using standard glovebox and Schlenk-line techniques. Using the method previously reported by Kakuchi et al. The ROP of *ɛ*-CL catalyzed by DPP (1 mol % with respect to monomer) was carried out in dry toluene at ambient temperature using 1,4-BDO as the initiator. In the glovebox in a clean dry Schlenk flask fitted with a stirrer bar, ε -CL (10 g, 87.6 mmol) was dissolved in 100 mL of dry toluene before the addition of neat 1,4-BDO (77.6 $\mu\text{L},\,8.76\,\times\,10^{-1}$ mmol) and a freshly prepared stock solution of DPP (219 μ L, 8.76 \times 10⁻¹ mmol, 1 mg μ L⁻¹ dry toluene stock). The Schlenk flask was sealed and removed from the glovebox and the polymerization was allowed to proceed with stirring until completion. The reaction was quenched and the catalyst removed with washed basic amberlyst resin. The resin was removed via gravity filtration and the PCL was recovered via precipitation from hexane before being filtered and dried in vacuo. The macroinitiator was dissolved in CH₂Cl₂ and dried over activated 3 Å molecular sieves using standard Schlenk-line techniques. The solvent was removed under reduced pressure and the dry macro-initiator was stored in the glovebox. Analysis was consistent with previous reports. (8.8 g, yield: 88%) ¹H NMR (400 MHz, CDCl₃) δ 4.07 (t, ${}^{3}J_{H-H} = 6.7$ Hz, 2H), 2.32 (t, ${}^{3}J_{H-H} = 7.5$ Hz, 2H), 1.76–1.59 (m, 4H), 1.46–1.34 (m, 2H). 13 C NMR (101 MHz, CDCl₃) δ 173.54 (s, C=0), 64.14 (s, CH₂), 34.12 (s, CH₂), 28.35 (s, CH₂), 25.53 (s, CH₂), 24.57 (s, CH_2).

Thermal Analysis

All triblock copolymers were analyzed by DSC and TGA to define the effect of chemical composition on thermal and degradation properties. DSC heating and cooling cycles were run in triplicate in series between -100 and $150 \,^{\circ}$ C under a nitrogen atmosphere at a heating rate of $+/-10 \,^{\circ}$ C min⁻¹ in a 40 μ L aluminum crucible. TGA was conducted between 20 and 300 $^{\circ}$ C at a heating rate of $10 \,^{\circ}$ C min⁻¹.

Tensile Analysis

All triblock copolymers, which could form "dog-bone" molds were analyzed using an M100-1CT tensiometer to determine the tensile properties of the materials. Molten polymer samples were molded into "dog-bones" via compression molding at 100 °C using a PTFE mold and allowed to cool to ambient temperature. The rate of elongation of each sample was 5 mm min⁻¹. Data was collected from ten repeats.

RESULTS AND DISCUSSION

Synthesis and Organocatalyzed ROP of PTO

As has been previously reported in literature,^{47,48} the acidcatalyzed acetal formation between benzaldehyde and pentaerythritol and subsequent ring-closure of the resultant diol with ethyl chloroformate offered a facile and good yielding route to achieve functional cyclic carbonate monomers





SCHEME 1 Synthesis of PTO from pentaerythritol. (a) Benzal-dehyde, HCI, deionized H_2O_1 80–25 °C. (b) Ethyl chloroformate, Et₃N, THF, 0–25 °C.

(Scheme 1). The use of deionized water as the reaction solvent in the synthesis of 1 allows for the synthesis of solely the monofunctionalized product. This is a consequence of the increased hydrophobicity of **1** causing the diol to precipitate from solution at room temperature and preventing any further protection. The synthesis of the benzylidene acetal monoprotected pentaerythritol and the subsequent ringclosure with ethyl chloroformate can be easily monitored by ¹H NMR spectroscopy. The appearance of a multiplet at δ = 7.45–7.31 ppm and a singlet at δ = 5.40 ppm is attributed to the formation of the benzylidene acetal while the loss of the doublet at δ = 4.58 ppm, attributed to the protons of the diol, and the shift of the two singlets attributed to the two methylene groups adjacent to the carbonate are indicative of the monomer formation (Supporting Information Fig. S2). The loss of the alcohol functionality can also be determined via infra-red spectroscopy in conjunction with the appearance of the carbonyl functionality attributed to the cyclic carbonate.

The organocatalyzed ROP of PTO was initiated from 1,4-butanediol (1,4-BDO) in CDCl₃ at ambient temperature ($\sim\!25$ $^\circ\text{C}$) and allowed for the synthesis of well-defined polymers.

TABLE 1 PPTO Homopolymer Data as Determined by GPC and

 ¹H NMR Spectroscopy

[<i>M</i>] ⁰ /[<i>I</i>] ⁰	Monomer Conversion ^a (%)	<i>M</i> n ^a (kg mol ⁻¹)	Mn ^b (kg mol ^{−1})	${\mathcal D}_{M}{}^{b}$
10	98	2.5	2.1	1.19
20	94	4.7	4.2	1.17
50	91	11.4	10.5	1.12
100	93	23.3	21.1	1.09
250	89	55.6	50.8	1.10

^a Determined by ¹H NMR spectroscopy.

 $^{\rm b}$ Determined by GPC analysis in ${\rm CHCl}_3$ against poly(styrene) (PS) standards.



FIGURE 1 Plot of M_n (GPC) against monomer conversion (¹H NMR spectroscopy) for PPTO homopolymerization ($[M]_0/[J]_0 = 100$, using 1 mol % DBU/5 mol % TU catalyst loading and 1,4-BDO as the initiator).

The resultant polymers displayed low dispersities $(\mathcal{D}_{\rm M} = 1.09 - 1.19)$ at a range of degrees of polymerization (DP = 10, 20, 50, 100, and 250) which is indicative that minimal adverse side reactions, such as transesterification, occur during the ROP (Table 1, Fig. 1, Supporting Information Fig. S3). The monomer conversion was monitored by ¹H NMR spectroscopy exploiting the shift from $\delta = 5.42$ to 5.35 ppm of the benzylidene proton adjacent to the acetal when polymerized. The number-average molecular weight (M_n) was plotted against percentage monomer conversion, determined by ¹H NMR spectroscopy, and was found to progress in a linear fashion, which indicates that the polymerization is occurring in a controlled manner as expected by ROP (Fig. 1). The utilization of a silica "plug" for polymer purification offered a facile method for the complete removal of the basic organocatalysts and residual monomer without acid-quenching, which may catalyze acetal-cleavage. The polymer was loaded onto the silica using CH₂Cl₂ as the eluent, removing residual monomer and TU ($R_f = 0.8$ and $R_f = 0.9$, respectively), before switching the eluent to ethyl acetate to recover the polymer



SCHEME 2 A-B-A triblock copolymer synthesis. (a) 1,4-BDO, DPP, toluene, and room temp.; (b) PTO, DBU, TU, and CH_2CI_2 , room temp.



FIGURE 2 GPC RI traces of PCL ($M_n \text{ NMR} = 30 \text{ kg mol}^{-1}$) based A-B-A triblock copolymers.

 $(R_{\rm f} = 0.9)$ whilst the DBU remained on the silica $(R_{\rm f} = 0)$. The polymer was recovered from solution *in vacuo* and displayed no observable degradation or acetal cleavage.

Synthesis of A-B-A Triblock Copolymers

The DPP-catalyzed ROP of ε -CL in toluene, previously reported by Kakuchi *et al.*¹², was initiated from 1,4-BDO at ambient temperature (~25 °C) to yield α,ω -dihydroxy PCL ranging in molecular weights (M_n NMR = 14 – 30 kg mol⁻¹) with low dispersities ($\mathcal{D}_M = 1.1 - 1.3$) (Supporting Information Fig. S4). The use of Amberlyst A21 basic resin offered a facile method of catalyst quenching and removal which was found to have no adverse effect on the resultant polymers.

The dihydroxy PCLs were dried in CH_2Cl_2 solution over 3Å molecular sieves and used as a macroinitiator for the ROP of PTO using the DBU/TU dual-organocatalytic system as described previously for the homopolymerization of PTO (Scheme 2). The system allowed for the synthesis of well-defined A-B-A triblock copolymers, with narrow dispersities (Fig. 2), displaying the versatile and selective nature of the dual-catalytic system in regards to the usage of ester-

TABLE 2 (Comparison	of PCL/F	РТО А-В-А	Triblock	Copoly	/mers
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containing macroinitiators with no observable adverse side reactions. The purification of the resultant materials via a silica "plug", optimized for the PPTO homopolymers, again allowed for the facile removal of residual monomer and catalyst without the use of strong acidic conditions, which may cleave the benzylidene acetal side group.

To determine the structure-property relationship of the A-B-A triblock materials, a library was constructed with varying weights of PCL "soft" midblock and PPTO "hard" terminal blocks (Table 2). In each case, the ROP chain extension allowed for the formation of well-defined polymers with decreasing dispersities as weights of hard block added increased.

Thermal and Mechanical Analysis of A-B-A Triblock Copolymer Library

The triblock copolymers were analyzed by DSC with the thermal cycles being performed consecutively in triplicate between -100 and $150 \,^{\circ}$ C at a rate of $+/-10 \,^{\circ}$ C min⁻¹.

As has been previously reported by Albuerne et al.,⁵⁰ each of the PCL homopolymers was observed to display a high degree of crystallinity, with $T_c = \sim 34$ °C, attributed to the alignment of the PCL chains. Furthermore, it was noted that the percentage crystallinity of the PCL homopolymers significantly reduced with increasing molecular weight (Table 2) as a consequence of long-chain entanglement retarding the nucleation process, as is explained in reptation-nucleation theory.⁵¹

The presence of two glass transition temperatures in the DSC thermograms at -58 and 70 °C are attributed to the PCL and PPTO blocks respectively (Fig. 3). The appearance of both glass transition temperatures is indicative of the bulk microphase separation of the A-B-A system. The DSC thermograms of the triblock copolymers also display a further reduction in the crystallinity of the PCL midblock which was found to be inversely proportionate to the PPTO chain length. This may be a result of the microphase separation of

Polymer	PCL <i>M</i> n _{NMR} ^a	PPTO <i>M</i> n _{NMR} ^{a,b}	Weight % PPTO ^c	<i>M</i> _n GPC (kg mol ^{−1}) ^d	${D_{M}}^{b}$	Strain at Break (%) ^e	<i>E</i> (MPa) ^e	PCL T _c (°C) ^f	PCL Crystallinity (%) ^f
1	14,000	0	0	24.2	1.10	-	-	33.6	52.3
2	14,000	5,000	41.7	27.7	1.09	_	_	17.0	32.5
3	22,000	0	0	43.0	1.30	_	_	33.6	50.0
4	22,000	5,000	31.3	46.3	1.19	$\textbf{9.5} \pm \textbf{21.5}$	190.3 ± 5.5	27.2	42.1
5	30,000	0	0	52.7	1.32	$\textbf{70.4} \pm \textbf{26.2}$	$\textbf{176.4} \pm \textbf{7.3}$	33.6	46.2
6	30,000	4,250	22.0	56.1	1.30	548.9 ± 37.0	151.8 ± 8.7	28.8	37.6
7	30,000	14,000	48.3	68.9	1.14	407.4 ± 59.7	$\textbf{162.1} \pm \textbf{8.0}$	26.4	34.3
8	30,000	16,500	52.4	72.1	1.13	$\textbf{340.0} \pm \textbf{22.7}$	$\textbf{193.9} \pm \textbf{6.9}$	24.7	32.7

^a Determined by ¹H NMR spectroscopy.

^b Total $M_{\rm n}$ of PTO component.

 $^{\rm c}$ Weight % of PPTO calculated from $\it M_{\rm n}$ values determined by $^{\rm 1}{\rm H}$ NMR spectroscopy.

^d Determined by GPC analysis in DMF against poly(methyl methacrylate) (PMMA) standards.

^e Determined by tensiometric analysis (average of 10 samples, see Supporting information).

^f Determined by DSC.





FIGURE 3 DSC thermograms. PCL $(M_n \text{ NMR} = 30 \text{ kg mol}^{-1})$ based A-B-A triblock 8 (Table 2, cooling cycle), (bottom) expansion of glass transition of PPTO hard-segment. Heat flow; endotherm down.

the A and B blocks further preventing the alignment and nucleation of the PCL midblock. The thermogravametric analysis of the triblocks further confirms the presence of 2 polymeric species through the presence of 2 discrete inflections at 318 and 389 °C which reveal that the PPTO block degrades prior to that of the PCL block, which under the same conditions begins thermal degradation at 389 °C (Supporting information Figs. 18).

The tensile properties of the A-B-A triblock copolymers and the PCL macroinitiators were investigated to deduce the effect of the reduction of the PCL crystallinity and the microphase separation within the material on the overall mechanical properties. As a consequence of their brittle nature, triblocks incorporating PCL macroinitiators in which $M_{n \text{ NMR}} = 14 \text{ kg mol}^{-1}$ were unable to be molded for analysis.

In the case of both PCL homopolymer (5, $M_{n \text{ NMR}} = 30 \text{ kg}$ mol^{-1}) and triblocks (6, 7, 8) consisting of PCL $M_{\rm n \ NMR} = 30 \text{ kg mol}^{-1}$, at low strains, a linear response was observed on the stress-strain curves before deformation or "necking" occurred (Fig. 4). Consistent with previous reports,⁵² the PCL homopolymer was observed to be a relatively stiff material (E = 176.4 MPa) displaying poor elongation with a tendency toward "necking" under low strain $(\sim 70\%)$. The addition of PPTO terminal blocks led to a significant improvement in the elongation of the materials being observed. It was found that the addition of PPTO blocks with a $M_{\rm n NMR} = 4.25 \text{ kg mol}^{-1}$, ~12.5 wt % of the overall polymer composition, that the strain of the material increased from 70% to 549%. It was also noted that the Young's modulus (E) of 6 was lower in comparison to the PCL homopolymer. It is postulated that this reduction in E is a result of the decreased crystallinity of the midblock region, while the improvement in elongation may be attributed to the microphase separation of the relatively small terminal block constituent creating an "anchoring" effect for the amorphous region. Notably it was found that E, although initially reducing after the addition of PPTO in comparison to PCL homopolymer, was found to be proportional to molecular weight of the PPTO blocks. Furthermore, the strain at break of the materials was found to be inversely proportional to the molecular weight of the PPTO blocks. As a consequence of the PPTO segments constituting a higher weight percentage of the overall polymer composition, the mechanical properties become more dependent on the hard block. Comparison of the wt % PPTO block to both strain at break and Young's modulus for materials with at 30 kg mol⁻¹ PCL block (see Supporting information) confirms this observation, demonstrating that increasing PPTO wt % leads to decreasing strain at break. It was also



FIGURE 4 Stress-strain curves of triblocks 4–8 (Table 2). Experiments were conducted at ambient temperature (\sim 25 °C) and 5 mm min⁻¹ until failure.

observed that A-B-A triblock **7** displayed a comparable Young's modulus to the PCL homopolymer but with a vastly superior elongation before failure with no observable "necking." The point of plastic deformation of triblock **8** (17 MPa) was also found to be superior to that of the PCL homopolymer (14 MPa).

CONCLUSIONS

In conclusion, it was found that the utilization of the bifunctional organocatalytic system of DBU/TU in the ROP of PTO yielded well-defined homopolymers, free of any adverse side reactions, even at monomer conversions >90%. Using the well-controlled ROP system, it was possible to synthesise high $T_{\rm g}$ poly(carbonate)s, which could be further used in degradable biomaterials. As an example of such materials, the synthesis of PPTO-PCL-PPTO triblock copolymers were investigated and shown to yield a thermoplastic "hard-soft" material that displays superior tensile properties to the corresponding PCL homopolymer while retaining its low thermal processing temperatures. The ROP of pentaerythritol-based cyclic carbonates offers a simple synthetic route into degradable high $T_{\rm g}$ polymers for utilization in improving the tensile properties of low $T_{\rm g}$ poly(ester)s through micro-phase separation.

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