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# Unsaturated poly(ester-urethanes) with stereochemically-dependent thermomechanical properties

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ABSTRACT

Polymer crystallinity is known to be dependent upon backbone stereochemistry and this concept has emerged as an effective means of altering bulk material properties. Herein, we describe a simple, step-growth polymerization to synthesize unsaturated poly(ester-urethane)s using the thiol-Michael addition reaction. The absolute control of alkene stereochemistry (0−100 % *trans* content) in the polymer backbone was achieved by varying the *cis*/*trans* double bond content of the monomer feedstock. In turn, the crystallinity of the polymer was systematically varied which manifested in control over the resultant tensile properties such as Young's modulus, ultimate tensile strength and elongation at break. Generally, the crystallinity and tensile strength were positively correlated with increasing *trans* double bond content within the polymer.

**Introduction**

High performance elastomeric materials are widely exploited in a diverse range of applications such as aerospace, tissue engineering and wearable electronics.[1-3] The ability to systematically control the mechanical and thermal properties of materials through modification of the chemical structure within polymers is hence of high importance. In most synthetic polymeric materials, this control is achieved by changing the chemical nature of the monomers such that increased chain length, backbone stiffness or altering functional groups. In contrast, Nature's polymers use fewer building blocks but impart an additional complexity to the structure-property relationship by leveraging stereochemistry.[4-6] Fully harnessing the structural complexity of biopolymers remains elusive but, the manipulation of thermomechanical properties is an achievable target with the use of stereochemistry.[6] While the stereochemical dependence of mechanical properties within synthetic materials such as polylactide and vinyl polymers such as polypropylene are long established,[7-12] much less work has focused on the application of *cis*/*trans* stereochemistry within the polymer backbone to control the materials' properties.

The presence of *cis*/*trans* stereoisomerism in both ring systems and double bonds has been used to create polymers in which the thermomechanical properties are controlled by the stereochemistry of the monomer unit. Use of conformationally-locked rigid-rings, such as isohexides or cyclohexylene has been harnessed to create polyesters and polyurethanes through scalable polycondensation routes.[13-18] While incorporation of these groups results in stereochemically-dependent thermomechanical properties, the molecular weights of the resultant polymers are generally modest ($M_w$ < 100 kDa), thus limiting their mechanical properties.

Double bond stereochemistry within polymer backbones is known to lead to dramatic changes in thermomechanical properties and is exemplified by polyisoprene (natural rubber or gutta-

percha) and its analogues.[19-21] Synthetically this is primarily achieved through the application of maleic and fumaric acids to polymer systems,[22-24] however, the extreme conditions that are required in polycondensation (reaction temperatures > 200 °C) typically leads to some isomerization of the monomers and/or polymers.[25] A recent example yielded 1,4 butandiol-maleate copolymers at a moderate molecular weight ($M_w$ = 32 kDa) *via* step-growth polymerization.[26] Whilst the thermomechanical dependence on the polymer stereochemistry was clear, unwanted isomerization at polymerization temperatures (>140 °C) led to loss of stereo-purity of the double bond in the polymer backbone.

More recently, some of us have reported that polymers with stereochemically-controlled double bonds in their backbone can be accessed through a simple nucleophilic thiol-yne addition to afford high molecular weight ($M_w$ > 100 kDa) polymers.[27] Here, the stereochemistry was dictated by the reaction polarity and the basicity of the amine catalyst enabling control of the *cis* content between 32−80%.[28] Despite the demonstration of stereochemically-dependent thermomechanical properties, the ability to access materials with higher levels of stereospecificity remained elusive.

Herein, we present a simple protocol to afford unsaturated polymers with absolute control over alkene stereochemistry through the application of monomers with pre-defined stereochemistry with the absence of isomerisation (Scheme 1). Using a room temperature thiol-Michael addition to achieve a step-growth polyaddition,[29-33] the *cis*/*trans* double bond content of the polymers was controlled by simply controlling the feed ratio of monomers. The stereochemical definition of the polymer controlled the crystallinity and, subsequently, the thermomechanical properties of the resultant materials.
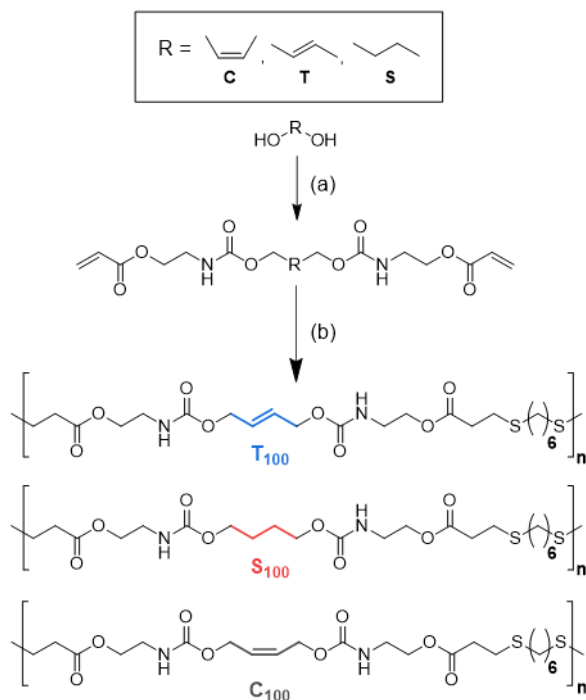
**Scheme 1.** Synthesis of poly(ester-urethane)s from saturated and stereo-defined diols.

(a) 2.1 equiv. 2-isocyanatoethyl acrylate, 0.2 mol% dibutyl tin(IV) dilaurate, THF, 22 °C. (b) 1 equiv. of 1,6-hexandithiol, 2 mol% dimethylphenylphosphine (DMPP), DMF, 22 °C. Homopolymers denoted as $X_{(\% \text{ molarity of diacrylate in polymer})}$, where X is C, T, S for *cis*, *trans*, saturated (for example, saturated homopolymer = $S_{100}$).

*Homopolymer synthesis and characterization* We envisioned a simple protocol to afford alkene-containing monomers suitable for step-growth polymerization. Four-carbon unsaturated diols (*cis* or *trans*) and a saturated diol were reacted with a commercially available isocyanate to afford di-acrylate monomers − *cis* (**C**), *trans* (**T**), and saturated (**S**) – that were suitable for step-growth polymerization. Initially, the di-acrylates were reacted with 1,6-hexanedithiol in the presence of a phosphine catalyst to yield high molecular weight ($M_w$ > 100 kDa) polymers (Scheme 1, Supporting information). Notably, ^{1}H NMR spectroscopic analysis of the polymers indicated complete stereochemical retention along the backbone (Figure 1).

Polymer films for mechanical testing were prepared by melt processing the polymers under pressure (6.24 MPa) between 90 - 120 °C for 10 min.  The polymers remained soluble after processing which indicated that no significant crosslinking had occurred and $^1$H NMR spectroscopic analysis of the processed samples confirmed no appreciable isomerization of the alkene units, thus highlighting their robust thermal stability. Each film was annealed for 7 d at 23 °C in an incubator to ensure thermal equilibration before the thermomechanical properties and characterization were assessed on annealed films (Figure 1).
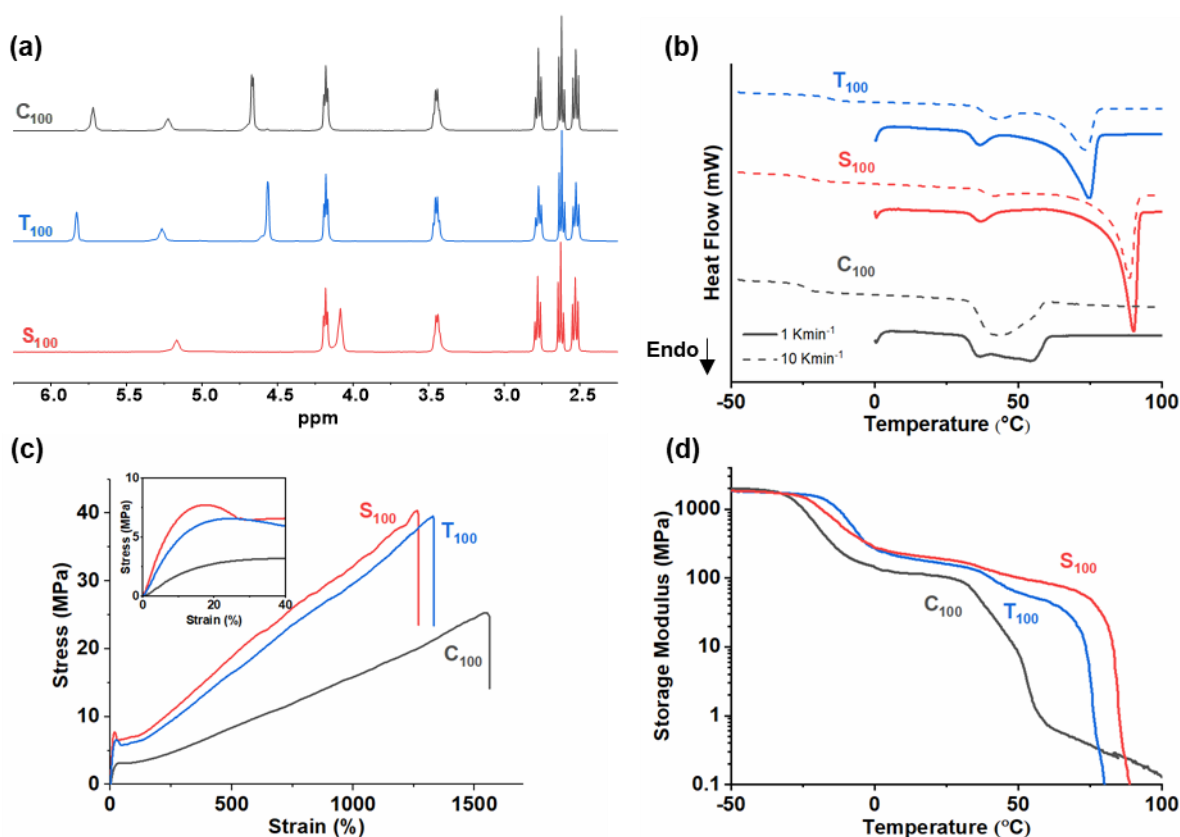


**Figure 1.** (a) $^1$H NMR spectra of homopolymers in CDCl$_3$ (400 MHz, 298 K); (b) Differential scanning calorimetry thermograms of homopolymers for 1$^{st}$ heating cycle (dashed lines = 10 K·min$^{-1}$ and solid lines = 1 K·min$^{-1}$); (c) Representative stress *vs* strain plot of 7 day annealed homopolymers (n = 5), *Inset* data between 0 - 40% strain; (d) Dynamic mechanical thermal analysis thermograms of storage modulus *vs* temperature performed in tensile configuration (frequency = 1 Hz, 2 K·min$^{-1}$. Representative curve shown, n = 3).

To separate molecular chain entanglements from the tensile properties of the system, rheology was performed. Isothermal frequency sweeps were performed on the homopolymers in order to calculate entanglement molecular weight ($M_e$) using polydisperse double reptation theory (SI figure 25 and Table 1).[34] All homopolymers possessed low $M_e$ values that suggests all samples contain a high level of entanglement. **C100** possessed a marginally higher $M_e$ indicating the geometry of the double bond affects the entanglements of linear polymer systems.

The mechanical tests show that **T100** and **S100** are both tough plastics with good ductility. Both possess similar tensile properties. In contrast, **C100** has a comparatively lower Young's modulus with a higher elongation at break, but it features a lower ultimate tensile strength (UTS). These results show that the stereochemistry of the double bond successfully controls the mechanical properties of the polymeric materials. Similarly to the relationship the stereochemistry of its double bond and mechanical properties of polyisoprene, the planarity of the backbone is disrupted by the *cis* configuration which precludes efficient chain packing to yield a more disordered system that is softer and more flexible. This disruption in the chains can be further understood by infrared (IR) analysis of hydrogen bonding in the homopolymers.
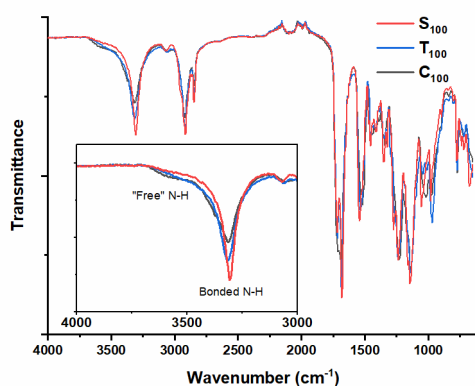


**Figure 2.** IR spectrum of fabricated homopolymer films *Inset* data between 3000 – 4000 cm$^{-1}$ (N-H region).

Analysis of the IR spectra reveal two distinct signals for the N-H moieties in urethanes, hydrogen bonded and "free" N-H bonds at a slightly higher wavenumber.[35] The observed IR frequency of the homopolymers reveals a sharp signal (3310 cm$^{-1}$) that is indicative of hydrogen bonding and a broad shoulder (~3590 cm$^{-1}$) that is indicative of "free" N-H bonds. Increased broadness and a reduction in the intensity of the hydrogen bonding signal (3310 cm$^{-1}$) in the **C$_{100}$** spectrum indicates that a lower amount of hydrogen bonding is present in the system in comparison to **T$_{100}$** and **S$_{100}$** (Figure 2).

Inevitably, with varying levels of hydrogen bonding and chain packing, investigating the crystallinity of this system will help to further elucidate stereochemistry's influence to the polymer properties. Thus, we investigated the thermal properties of the polymers to assess the degree of crystallinity in each system.

**Table 1. Thermal and tensile data of annealed homopolymers**

| | $M_n{}^a$ (kDa) | $M_w{}^a$ (kDa) | $Đ_M{}^a$ | $M_e{}^b$ (kDa) | $T_g{}^c$ (°C) | $T_m{}^c$ (°C) | $\Delta H_m{}^c$ (J·g$^{-1}$) | $E^d$ (MPa) | $\sigma_b{}^e$ (MPa) | $\varepsilon_b{}^f$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| S$_{100}$ | 30.8 | 139 | 4.51 | 2.12 | -19 | 90.2 | -41.3 | 81±8 | 37±2.7 | 1191±76 |
| T$_{100}$ | 26.0 | 103 | 3.57 | 2.01 | -14 | 74.6 | -37.2 | 66±11 | 39±8 | 1232±96 |
| C$_{100}{}^*$ | 29.0 | 250 | 7.19 | 3.23 | -18 | - | -27.0 | 25±4 | 23±2 | 1481±53 |

(a) $M_w$ and $Đ_M$ were determined by size exclusion chromatography (DMF, 0.5% w/w NH$_4$BF$_4$) analysis against poly(methyl methacrylate) (PMMA) standards. (b) Calculated from the fitting of polydisperse double reptation theory to TTS master plots (Figure S25) (c) The $T_m$ was taken as the minimum of the final transition, $T_g$ was obtained from 2$^{nd}$ heating cycle, total enthalpy of melting ($\Delta H_m$) was calculated by integration of all endothermic transitions from DSC thermograms; (d) Young's modulus; (e) Stress at break; (f) Strain at break (n=5). Uncertainty is presented as the standard deviation of samples. *Sample C$_{100}$ had multiple melt transitions that were indistinguishable at the heating rate.

***Homopolymer thermal properties.*** The thermal properties of each homopolymer were assessed by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). Initial DSC thermograms were obtained at a heating and cooling rate of 10 K·min$^{-1}$, however upon

observation of melt transitions, samples were tested at 1 K·min$^{-1}$ to increase the resolution of the multiple thermal transitions. Each homopolymer displayed melt transitions ($T_m$) in the first heating cycle of the DSC thermogram which indicates that each material is semi-crystalline in nature.[36] Unsurprisingly, **T$_{100}$** and **S$_{100}$** possess comparable melt temperatures (with two distinct transitions), total melting enthalpy ($\Delta H_m$) and DSC thermogram profiles (Figure 1−C). Once again, the **C$_{100}$** sample was drastically different. Specifically, a broad melting profile with multiple transitions was observed and the $\Delta H_m$ was significantly smaller (Figure 1-C, Table 1). Since $\Delta H_m$ can be correlated to bulk crystallinity, the relative crystallinity for the polymers was determined to be **S$_{100}$** > **T$_{100}$** >> **C$_{100}$**. Furthermore, the polymer crystallinity was positively correlated with Young's Modulus and negatively correlated with elongation at break (Figure 1-B, Table 1). Unusually, all the homopolymers possessed multiple melt transitions; this phenomenon is not commonly observed for alternating copolymers and is more commonly seen in materials that possess a distinct segmental structure (*e.g.* block or multiblock copolymers).[37-38] In a previous study of semi-crystalline materials possessing a similar thermal profile, the lower temperature melt transition was correlated to short range crystalline ordering and the higher temperature transitions to overall longer range order in the system.[36, 39] Comparing **C$_{100}$** and **T$_{100}$** (or **S$_{100}$**) it is possible that the disorder introduced by the *cis* moiety prevents the longer range order that may be observed in the latter. The morphology of these non-segmented polyester-urethanes are currently being studied using microscopy.

DMTA was used to further analyze the thermomechanical properties of the homopolymers in which samples of annealed polymer films were subjected to thermal sweeps in the tensile mode. For each polymer, three distinct phases were apparent which correspond to the glassy-state at low temperatures (storage modulus > 1 GPa), followed by a wide rubbery plateau above the glass

transition and polymer flow at the respective melt transition. For the storage modulus, a considerably larger decrease is observed in the $C_{100}$ sample in comparison to the other derivatives which is intuitive for a softer sample at room temperature. The final decrease in storage modulus is characteristic of melting and this corroborates well with the melting transitions observed in the DSC thermograms. Another feature of interest is a slight decrease in storage modulus between the rubbery plateau and melting event that is only observed in $T_{100}$ and $S_{100}$. The temperature of this DMTA transition occurs roughly at the same temperature as the first melt transition in the DSC thermograms. This softening of material once a melt transition is reached could indicate the possibility of phase separation, whereby a phase losing its crystallinity reduces the influence on the materials' bulk properties.[23]
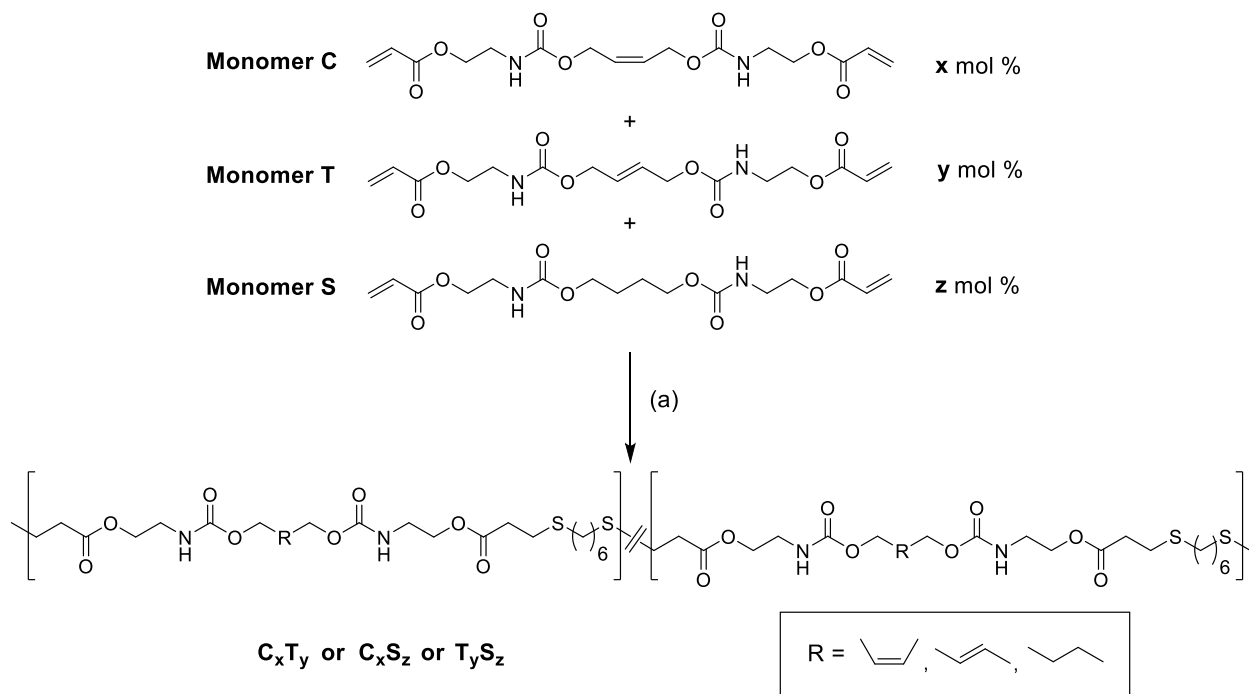


**Scheme 2.** Synthesis of random copolymers from di-acrylate monomers (a) 1 equiv. of 1,6-hexandithiol, 2 mol% of DMPP, DMF at 22 °C.

*Copolymer and blend preparation* Since the stereochemistry is fully retained in the final polymer, the monomer feed ratio can be used to precisely target the *cis/trans* content of the

resultant polymers. By varying the monomer feed ratio in a copolymerization of mixed monomers (*e.g.* monomers **C/T** or monomers **C/S**), random copolymers with various *cis* content were synthesized in an effort to manipulate the thermomechanical properties (Scheme 2). $^1$H NMR spectroscopic analysis of the copolymers indicated that the stereochemical ratio in the feedstock was undisturbed in the isolated polymer (see Supporting Information). A 1:1 **blended sample** of $C_{100}$ and $T_{100}$ homopolymers was fabricated into a thin film to assess any differences to the analogous copolymer sample.
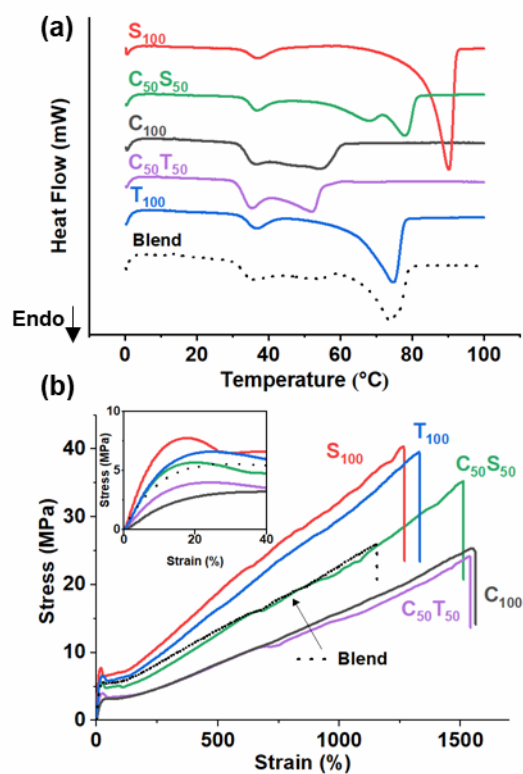


**Figure 3.** Representative uniaxial extension and thermal properties of 7 day annealed copolymers and a *cis*/*trans* blend. (a) First heating cycle DSC thermograms of annealed copolymers at a heating rate of 1 K·min$^{-1}$ (b) Stress *vs* strain plots of representative samples from the annealed copolymers at a strain rate of 10 mm·min$^{-1}$ *Inset* data between 0 - 40% strain.

***Copolymer and blend tensile testing*** The copolymers and blend were processed using the same conditions as the homopolymers, annealed for 7 d, and subjected to uniaxial tensile testing. The

**C₅₀S₅₀** copolymer sample displayed mechanical properties intermediate between the respective homopolymers, but it was found to have increased stiffness and possess higher toughness than **C₁₀₀**. Contrastingly, the mechanical properties of the *cis/trans* copolymer (**C₅₀T₅₀**) were almost identical to **C₁₀₀** which indicates that the mechanical properties of the sample were dominated by the packing of the *cis* double bond. Thus, in comparison to the *trans* double bond, the saturated linking unit had a stronger influence on final material properties at the same respective ratios. The blended material (50/50 mixture of **C₁₀₀** and **T₁₀₀**) appeared to have a larger Young's modulus compared to the **C₁₀₀** sample, but at the sacrifice of elongation at break and tensile toughness. Notably, the blend had a Young's modulus similar to the *trans* homopolymer (**T₁₀₀**); a stark contrast to the *cis*/*trans* copolymer (**C₅₀T₅₀**). The polymers were further subjected to thermal analysis in order to better understand the crystallinity of the system and elaborate on the mechanical trend (Figure 3).

**Table 2. Thermal and tensile data of random co-polymers and blend**

|  | $M_n$[a] | $M_w$[a] | $Đ_M$[a] | $T_g$[b] | $T_m$[b] | $\Delta H_m$[b] | $E$[c] | $\sigma_b$[d] | $\varepsilon_b$[e] | $U_T$[f] |
|---|---|---|---|---|---|---|---|---|---|---|
|  | (kDa) | (kDa | | (°C) | (°C) | (J·g⁻¹) | (MPa) | (MPa) | (%) | (MJ·m⁻²) |
| C₅₀S₅₀ | 34.9 | 209 | 5.99 | -19 | 77.9 | -35.9 | 53±7 | 33±3 | 1508±74 | 255±28 |
| C₅₀T₅₀ | 38.7 | 208 | 5.37 | -16 | 52.0 | -25.1 | 35±4 | 26±3 | 1558±75 | 199±27 |
| Blended (C₅₀T₅₀) | - | - | - | -17 | - | -37.0 | 52±8 | 25±3 | 1075±106 | 156±28 |

(a) $M_w$ and $Đ_M$ was determined by SEC (DMF, 0.5% wt/wt NH₄BF₄) analysis against poly(methyl methacrylate) (PMMA) standards; (b) The $T_m$ was taken as the minimum of the final transition, $T_g$ was obtained from 2ⁿᵈ heating cycle, Total enthalpy of melting ($\Delta H_m$) was calculated by integration of all endothermic transitions from DSC thermograms (Supporting Information); (c) Young's modulus; (d) Stress at break; (e) Strain at break; (f) Tensile toughness (n=5 except Blended sample where n=3). Uncertainty presented as the standard deviation of samples. An additional copolymer mixing the *trans* and saturated moiety (T₅₀S₅₀) was synthesized and data can be found in the Supporting Information. * Blended sample had multiple melt transitions that were indistinguishable at the heating rate.

*Copolymer and blend thermal properties*

The thermal properties of the copolymers and the blend were assessed by DSC analysis with a heating rate of 1 K·min$^{-1}$. The melt transitions observed in **C$_{50}$S$_{50}$** were shifted to higher temperatures and the total enthalpy of melting was larger than **C$_{100}$** indicating that the saturated linker resulted in increased crystallinity compared to when double-bond containing monomers were used (Figure 3-A). Simultaneously, increasing the *cis* double bond content disrupted the crystallinity enough to allow for a more ductile sample. A balance between the two competing moieties (*cis*−less ordered, saturated−more ordered) in **C$_{50}$S$_{50}$** is apparent in both thermal and tensile properties. Contrary to **C$_{50}$S$_{50}$**, the **C$_{50}$T$_{50}$** sample had a similar DSC profile and total enthalpy of melting as the purely *cis* containing **C$_{100}$**. This can be rationalized by the *trans* unit producing less order in the system than the saturated configuration, leading to the *cis* moiety within the backbone disrupting crystallization. Curiously, the blend had a similar DSC profile, total enthalpy of melting, and hence similar crystallinity, as the purely *trans* sample **T$_{100}$**. However the comparative copolymer **C$_{50}$T$_{50}$** was similar to the purely *cis* containing **C$_{100}$**. This demonstrates that incorporation of the *cis* moiety into a chain of crystalline *trans* units, as a copolymer, disrupts crystallinity while simple physical blending does not translate this disruption.

The clear manipulation of crystallinity and tensile properties observed in **C$_{50}$S$_{50}$** copolymer demonstrated that tensile enhancement was possible in copolymers. However the copolymers demonstrated that the *trans* double bond had negligible impacts on copolymer crystallinity at 50% content, and an increased amount of *trans* double bond content would be required to alter the thermomechanical properties.
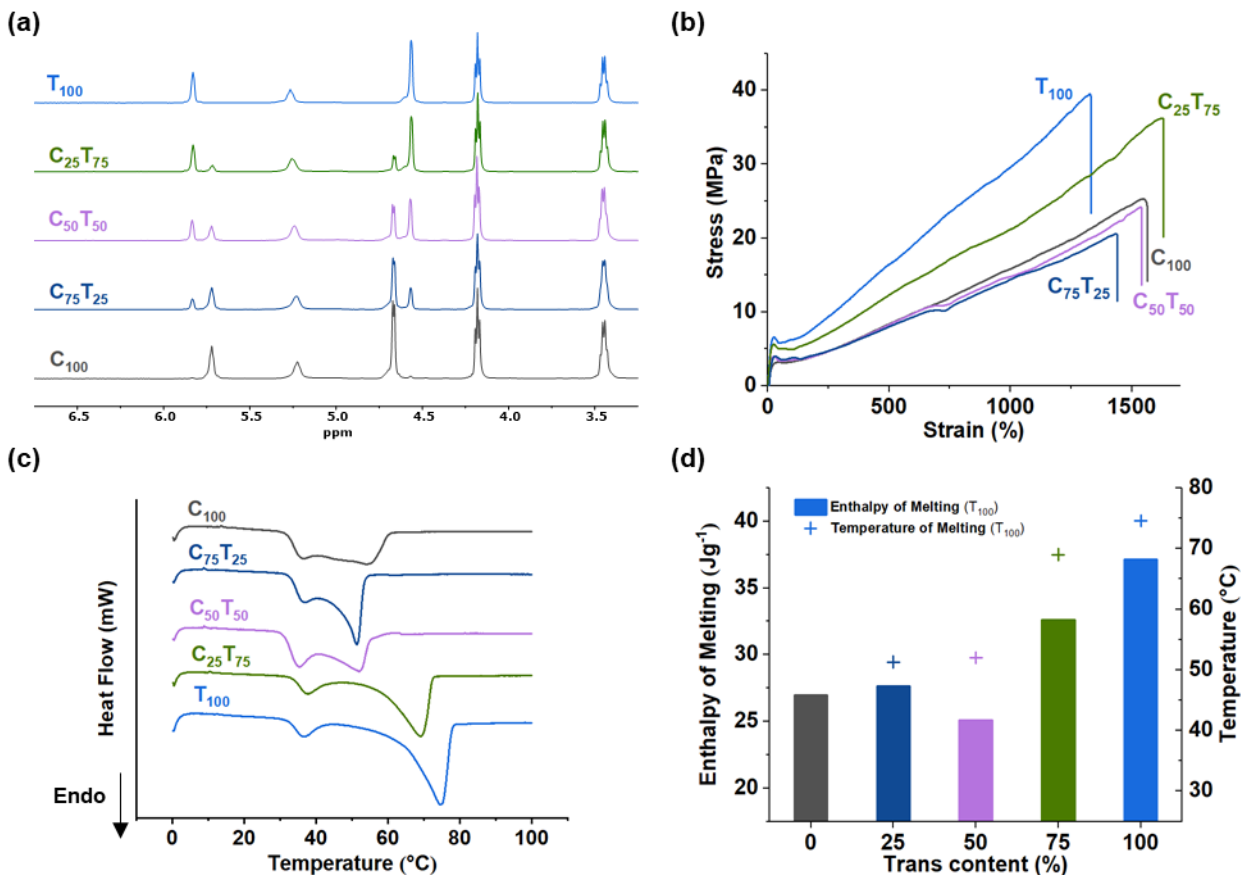
**Figure 4.** (a)$^1$H NMR spectra of stereocontrolled copolymers in (CDCl$_3$, 400 MHz, 298 K); (b) Representative stress *vs* strain curves of 7 day annealed copolymers; (c) DSC thermograms of stereocontrolled copolymers for 1$^{st}$ heating cycle at 1 K·min$^{-1}$; (d) Maximum melt transition peak and enthalpy of melting *vs trans* double bond content in stereo-controlled copolymers

*Stereocontrolled copolymers* In order to fully understand the effects of the *trans* double bond in a *cis/trans* copolymer system, more copolymers with various *cis/trans* ratios were prepared and tested using uniaxial tensile testing. Similarity among tensile properties is very apparent in samples containing 0 – 50% *trans* content since the UTS varies between 19 – 26 MPa and elongation at break only fluctuates from 1300 – 1500% (Figure 4). Compared to the 100% *cis* polymer (**C$_{100}$**), the polymer with 75% *trans* content (**C$_{25}$T$_{75}$**) is stronger ($\Delta UTS \sim 9$ MPa) and displays an increase of ~ 300% elongation at break compared with the 100% *trans* sample (**T$_{100}$**). Interestingly, the

slight deviation from linearity is reproducibly observed in the tensile curves, most notably for (**C₇₅T₂₅**). We attribute this to crystal slippage that is observed in some semi-crystalline systems. While this is more prevalent in polyolefin-based systems, there are some examples of more polar polymers displaying this behavior.[40-41] However, clearly alkene stereochemistry can be rationally leveraged to adjust bulk mechanical properties such as tensile strength, flexibility and elongation at break by simply adjusting monomer ratios in this simple system to afford copolymers with varied *cis/trans* content. It is interesting that mechanical properties of *cis/trans* copolymers are significantly different from respective homopolymers only when *trans* content > 50%, however *cis/*saturated materials display properties in between the respective homopolymers for the 50% system. We hypothesized that crystallinity was driving the observed differences in bulk properties for the *cis/trans* copolymers so we examined their thermal properties.

**Table 3. SEC characterization and tensile data for stereocontrolled copolymers**

| | $M_n$[a] | $M_w$[a] | $Đ_M$[a] | $T_g$[b] | $T_m$[c] | $\Delta H_m$[d] | $E$[e] | $\sigma_b$[f] | $\varepsilon_b$[g] | $U_T$[h] |
|---|---|---|---|---|---|---|---|---|---|---|
| | (kDa) | (kDa) | | (°C) | (°C) | (J·g⁻¹) | (MPa) | (MPa) | (%) | (MJ·m⁻²) |
| C₁₀₀ | 29.0 | 250 | 7.19 | -18 | - | -27.0 | 25±4 | 23±2 | 1481±53 | 174±17 |
| C₇₅T₂₅ | 35.4 | 194 | 5.30 | -17 | 51.3 | -27.6 | 35±5 | 19±3 | 1307±160 | 137±30 |
| C₅₀T₅₀ | 38.7 | 208 | 5.37 | -16 | 52.0 | -25.1 | 35±4 | 26±3 | 1558±75 | 199±27 |
| C₂₅T₇₅ | 31.8 | 129 | 4.18 | -15 | 69.0 | -32.6 | 46±6 | 30±4 | 1436±164 | 233±48 |
| T₁₀₀ | 26.0 | 103 | 3.57 | -14 | 74.6 | -37.2 | 66±11 | 39±8 | 1232±96 | 261±72 |

(a) $M_w$ and $Đ_M$ was determined by SEC (DMF, 0.5% wt/wt NH₄BF₄) analysis against poly(methyl methacrylate) (PMMA) standards. (b) The $T_g$ was obtained from 2nd heating cycle (Supporting Information). (c) The $T_m$ was taken as the minimum of the final transition. (d) Total enthalpy of melting ($\Delta H_m$) was calculated by integration of all endothermic transitions. (e) Young's modulus (f) Stress at break (g) Strain at break (h) Tensile toughness n=5. Uncertainty presented as the standard deviation of samples.

Analysis of the polymer samples by DSC revealed a positive correlation between *trans* double bond content and the melt transition. Specifically, the melting behavior became better resolved with the second melt transition shifting to increasingly higher temperature after 50% *trans* content was surpassed, while polymers containing ≤ 50% *trans* content had similar melting temperatures. The trend for total melt enthalpy was less clear since, the value remained relatively consistent for samples with ≤ 50% *trans* content before increasing significantly thereafter (Figure 4-C). Nonetheless, the crystallinity increased dramatically at 75% *trans* double bond content which indicates that the *trans* double bond becomes a dominating influence in controlling the crystallinity of the materials at this threshold. A similar "inflection point" has been observed around 50% *cis* content in other alkene containing polyesters.[28] However, it should be noted that the stereochemical trends were reversed for this case *i.e.* crystallinity and UTS increased with *cis* content. Further investigation of these polymers and/or the synthesis of alternative alkene-containing scaffolds can help to reconcile such disparities and provide a more rational platform for tuning thermomechanical properties.

**Conclusion**

A polymer system containing *cis/trans* alkene stereochemistry has been designed that can afford high molecular weight polymers without compromising stereochemical purity during polymerization and subsequent material processing. For the unsaturated polymers, the stereochemical content influenced the thermomechanical properties and this was further correlated to the degree of crystallinity within the sample. Polymer crystallinity is extremely important in the determination of thermomechanical properties and moreover, precision tuning of crystallinity can be challenging and often involves more demanding synthetic endeavors and/or drastic changes to

the resultant polymer microstructure. The manipulation of polymer alkene stereochemistry to modify bulk crystallinity presents a much more accessible path to materials possessing tunable stiffness, tensile strength and flexibility.

ASSOCIATED CONTENT

**Supporting Information**. Experimental details of monomer, polymer and co-polymer synthesis including NMR spectroscopy and SEC characterization. Full tensile, DSC and DMTA data for all synthesized polymers can be found as well as an additional synthesized polymer: $T_{50}S_{50}$. The following files are available free of charge.

"Experimental Data" PDF

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**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. C. J. S. performed all synthesis and thermomechanical

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ABBREVIATIONS

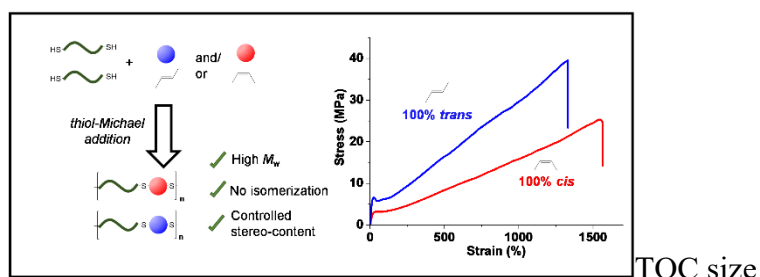| | |
|---|---|
| $M_w$ | Mass average molar mass |
| $M_e$ | Entanglement Molecular weight |
| $M_n$ | Number average molar mass |
| NMR | Nuclear Magnetic Resonance |
| SEC | Size Exclusion Chromatography |
| DSC | Differential Scanning Calorimetry |
| DMTA | Dynamic Mechanical Thermal Analysis |
| DMF | $N,N$-Dimethylformamide |
| PMMA | Poly(Methyl methacrylate) |
| UTS | Ultimate Tensile Strength |
| $T_g$ | Glass transition Temperature |
| $Đ_M$ | Dispersity |
| TGA | Thermal Gravimetric Analysis |
| THF | Tetrahydrofuran |
| TTS | Time-Temperature Superposition |
| WLF | Williams-Landel-Ferry |

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