STILBENE-CONTAINING THERMOTROPIC LIQUID CRYSTALLINE POLYESTERS FOR AEROSPACE APPLICATIONS
Ashley M. Nelson
Advisor: Timothy E. Long
Department of Chemistry, Macromolecules and Interfaces Institute
Virginia Tech, Blacksburg, VA 24061-0344

Abstract

Materials used in space travel must maintain thermal and dimensional stability in extreme conditions, while remaining melt processable for ease of industrial production. The rigid chemical structure of stilbene often correlates to polymers exhibiting a liquid crystalline morphology and the olefinic bond undergoes a $[2 + 2]$ cycloaddition in the presence of UV light. Based on the combined benefits of a non-destructive photocrosslinking reaction and liquid crystallinity, we propose the use of stilbene-containing (co)polyesters for various aerospace applications. These copolyesters include random copolyesters, and segmented copolyesters achieved using functional polyols. The synthesis and characterization of (co)polyesters containing 4,4’-dimethyl-trans-stilbene dicarboxylate (SDE), 1,6-hexanediol (HD), and 1,4-butanediol (BD) was performed. These (co)polyesters demonstrated thermal stability of greater than 360 °C and liquid crystalline morphologies, confirmed using polarized optical microscopy, with melting temperatures ranging from 253 – 196 °C. Dynamic mechanical analysis afforded moduli ~1000 MPa and tensile data resulted in a Young’s modulus of the same magnitude. Melt rheology was also performed and showed the characteristic shear thinning expected of liquid crystalline polymers. To investigate the effect of comonomer composition on the thermal transitions and liquid crystallinity, polyesters containing diols of varying alkyl spacer length and an aliphatic diol with stereochemistry were also synthesized.

Introduction

Thermotropic liquid crystalline polyesters are a unique class of high performance polymers that exhibit order during melt processing above the crystalline melting point. Mesogenic units, extended aromatic sequences, within the main chain promote the formation of this ordered morphology, often resulting in anisotropic, high modulus structures. These mesogenic units are typically either present in the backbone of the polymer or as pendant groups resulting in main-chain and side-chain liquid crystalline polymers respectively. Liquid crystalline polymers demonstrate outstanding dimensional stability at high temperatures, resistance to chemicals and corrosion, exhibit low dielectric constants, and high moduli over a wide temperature window. Liquid crystalline polymers also exhibit shear thinning during melt processing, which facilitates melt extrusion and injection molding for product formation. Based on these synergistic attributes, liquid crystalline polymers offer versatility in aerospace coatings, adhesives, displays, and structures.

Previous literature indicates that the incorporation of stilbene units into the polymer backbone results in liquid crystalline polymers, classifying stilbenes as mesogens. It is also established that stilbenes undergo a $[2 + 2]$ cycloaddition reaction in the presence of ultraviolet (UV) light. This reaction results in photo-induced crosslinking; a non-degradative process with the ability to provide enhanced thermomechanical properties. Utilizing both of these important characteristics allows the tailoring of polymers...
for specific applications. The objectives of this research were to synthesize high-performance liquid crystalline photocrosslinkable (co)polyesters containing 4,4'-dimethyl-trans-stilbene dicarboxylate (SDE) for use in aerospace applications and to investigate the effect of flexible versus rigid comonomers and copolymer composition on the liquid crystalline textures, thermal, and thermomechanical properties.

In the following, we describe the synthesis and characterization of high-performance photocrosslinkable (co)polyesters containing stilbene for use in aerospace applications. A variety of possible (co)monomer(s) are available and allows for the tailoring of polymers with specific thermal and thermomechanical properties. The synthesis and characterization of (co)polyesters containing 4,4'-dimethyl-trans-stilbene dicarboxylate (SDE), 1,6-hexanediol (HD), and 1,4-butanediol (BD) is discussed in detail. The specific characterization techniques include thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), polarized optical microscopy (POM), dynamical mechanical analysis (DMA), tensile testing, and melt rheology.

**Experimental**

**Materials**

1,6-hexanediol (97%), 1,4-butanediol (99%), 1,5-pentanediol (97%), and 1,8-octanediol (98%), and 1,10-decanediol (98%) were obtained from Sigma Aldrich and used as received. 1,4-cyclohexanediol (70:30 cis:trans) was obtained from Alfa Aesar and used as received. 4,4'-dimethyl-trans-stilbene dicarboxylate was generously supplied from Eastman Chemical Company and used as received.

**Analytical Methods**

1H NMR spectroscopy was obtained using a 400 MHz Varian Tecmag Apollo in a solvent mixture of pentafluorophenol and CDCl3 at ambient temperature. A TA Hi-Res TGA 2950 or Q500 provided polymer thermal weight loss under an inert atmosphere and a temperature ramp of 10 °C/min from 25 to 600 °C. DSC was performed using a TA Q1000 or Q2000 heat/cool/heat method with a heating ramp of 10 °C/min and a cooling rate of 100 °C/min. Melt rheological studies were performed on an AR2000 rheometer using 25 mm parallel plate geometry. A strain sweep was performed to determine the linear viscoelastic regime and the experimental temperature range was sample dependent. Compression molding at 275 - 315 °C between Teflon® sheets produced free-standing polymer films ~0.3 mm thick. DMA (TA Q800) provided thermomechanical properties of the polymer films under tension mode at a frequency of 1 Hz and a temperature ramp of 3 °C/min from 0 °C until the storage modulus reached less than 0.1 MPa. A Zeiss Axioplan polarizing optical microscope equipped with a THMS 600 hot stage afforded polarized optical micrographs of a thin polymer film. Films were mounted between two glass slides and images taken as the film was heated at a rate of 10 °C/min. Tensile testing was performed on the polymer films using an Instron 4411 with a crosshead speed of 0.5 mm/min. The tensile properties are represented as an average of five samples.

**Polymer Synthesis**

All polymers were synthesized using melt transesterification in a similar manner. The reaction setup consists of a round-bottom flask equipped with a mechanical stirrer, N2 inlet, and distillation apparatus. The following procedure describes the synthesis of poly(4,4'-dimethyl-trans-stilbene
dicarboxylate (SDE)-1,6-hexanediol (HD)). A dry 100 mL round bottom was charged with 8.4461 g (28.50 mmol) of SDE, 4.0401 g (34.19 mmol) of HD, and ~0.05 mL (40 ppm) titanium tetraisopropoxide. The reaction was purged with N₂ and degassed three times. The reaction, with a constant N₂ purge, was heated to 190 °C for 2 h. The temperature was then increased to 220 °C for 2 h and finally to 275 °C for 0.5 h. Vacuum was subsequently applied at 275 °C for 2 h. To solid-state (SS) the polyester, small pieces of the polymer were placed in an identical setup as described above and heated to 130 °C with stirring and constant N₂ purge for about 25 h.

**Results and Discussion**

**Molecular Weight Characterization and Solid-Stating Strategies**

Polymerization using a melt transesterification strategy was employed, a technique which eliminates solvent and results in direct isolation of the polyesters. Both attributes are critical principles of strategies for emerging green chemistry. **Scheme 1** shows the synthesis of a random copolyester system containing SDE, HD, and 1,4-butanediol (BD). As expected, these copolyesters were insoluble in any safe organic solvent, thus molecular weight characterization using common size exclusion chromatography (SEC) was unable to be performed. To quantitatively determine if substantial molecular weight was achieved, films were melt pressed. Increasing BD concentration resulted in brittle films due to the SDE-BD segments having such high melting points. Melt transesterification only works when the polymer is molten, therefore, when the melting temperature is above the final temperature reached in polymerization, high molecular weight is not always achieved.

**Scheme 1.** Synthesis of poly(SDE-HD)ₓ-co-poly(SDE-BD)ᵧ using melt transesterification.

To overcome the aforementioned downfall when preparing high melting polymers, strategies such as solid-state (SS) polymerization often follow. To SS the polymers are placed and held at a temperature above the glass transition temperature (T_g) but below the melting temperature (T_m) and either wicked with N₂ or held under reduced pressure for an extended period of time. **Figure 1** shows the complex viscosity vs frequency plot for the same poly(SDE-HD) sample before and after SS. The zero-shear viscosity is the initial complex viscosity measured at 0.1 Hz and compares between samples similar to molecular weights. Before SS the zero-shear viscosity was 12030 Pa·s and after it was 25930 Pa·s, confirming the increase in molecular weight obtained upon SS.

**Figure 1.** Complex viscosity of poly(SDE-HD) at 263 °C before and after SS.
Thermal Characterization and Liquid Crystallinity

Understanding the thermal limitations of these (co)polymers is of utmost importance because the desired applications require high working temperatures. The TGA curve for poly(SDE-HD), seen in Figure 2, depicts a one-step degradation profile with an onset of weight loss at 384 °C. Copolyesters charged with 10, 25, 50, 75, 90, and 100 mol % BD also exhibited one-step degradations and thermal stability of greater than 360 °C. DSC determined the effect of (co)polymer composition on the thermal transitions. Figure 3 depicts the DSC trace of poly(SDE-HD), which exhibited a melting temperature ($T_m$) of 253 °C and an isotropic temperature ($T_i$) of 284 °C. As the incorporation of BD increased, the $T_m$ depressed until the BD incorporation was greater than HD, resulting in higher $T_m$s and $T_i$s than the HD-rich analogs. Some compositions also displayed a crystallization temperature ($T_c$). The lower $T_m$, while maintaining similar $T_i$s, correlated to an increased mesophase stability ultimately lowering the required temperature for melt processing. Table 1 summarizes the thermal transitions for the various (co)polymers. POM images showed crystals above the $T_m$; further confirmation of the liquid crystalline morphology DSC suggested. Figure 4 shows images of poly(SDE-HD), poly(SDE-HD)$_{90}$-co-poly(SDE-BD)$_{10}$, and poly(SDE-HD)$_{75}$-co-poly(SDE-BD)$_{25}$ at 250 °C taken at 275, 270, and 250 °C respectively.

![TGA curve of poly(SDE-HD)](image)

![DSC trace of poly(SDE-HD)](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{d,onset}$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$T_i$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(SDE-HD)</td>
<td>384</td>
<td>--</td>
<td>253</td>
<td>284</td>
</tr>
<tr>
<td>poly(SDE-HD)$<em>{90}$-co-poly(SDE-BD)$</em>{10}$</td>
<td>364</td>
<td>213</td>
<td>237</td>
<td>286</td>
</tr>
<tr>
<td>poly(SDE-HD)$<em>{75}$-co-poly(SDE-BD)$</em>{25}$</td>
<td>405</td>
<td>189</td>
<td>218</td>
<td>285</td>
</tr>
<tr>
<td>poly(SDE-HD)$<em>{50}$-co-poly(SDE-BD)$</em>{50}$</td>
<td>377</td>
<td>--</td>
<td>196</td>
<td>292</td>
</tr>
<tr>
<td>poly(SDE-HD)$<em>{25}$-co-poly(SDE-BD)$</em>{75}$</td>
<td>395</td>
<td>248</td>
<td>265</td>
<td>323</td>
</tr>
<tr>
<td>poly(SDE-HD)$<em>{10}$-co-poly(SDE-BD)$</em>{90}$</td>
<td>400</td>
<td>--</td>
<td>276</td>
<td>328</td>
</tr>
<tr>
<td>poly(SDE-BD)</td>
<td>396</td>
<td>--</td>
<td>317</td>
<td>346</td>
</tr>
</tbody>
</table>

Table 1. Thermal transitions of various stilbene-containing (co)polymers.
Figure 4. Polarized optical micrographs of a) poly(SDE-HD), b) poly(SDE-HD)\textsubscript{90}-co-poly(SDE-BD)\textsubscript{10}, and c) poly(SDE-HD)\textsubscript{75}-co-poly(SDE-BD)\textsubscript{25} taken between the melting and isotropic transitions visually confirming the presence of a mesophase.

To further investigate the effect of the alkyl spacer length on the thermal transitions and liquid crystallinity, polyesters were synthesized with 1,5-pentanediol (PD), 1,8-octanediol (OD), and 1,10-decanediol (DD). As previously noted, the BD homopolymer showed an increased T\textsubscript{m} and T\textsubscript{i} compared to the HD. Figure 5 shows the thermal transitions exhibited by SDE homopolymers with PD, OD, and DD. Poly(SDE-PD) showed a lower T\textsubscript{m} and T\textsubscript{i} than both the BD and HD homopolymers. This is attributed to decreased crystallization and packing because of the odd spacer length.\textsuperscript{7} Both poly(SDE-OD) and poly(SDE-DD) displayed solely T\textsubscript{m}s, alluding to the non-liquid crystalline nature of these systems. The longer, more flexible nature of these alkyl spacers results in the loss of liquid crystallinity, as a rigid structure is required for the anisotropic nature to appear.\textsuperscript{7} In a similar manner, introducing a cycloaliphatic monomer with stereochemistry, 1,4-cyclohexanediethanol (70:30 \textit{cis}:trans) (CHDM), resulted in a high melting polyester, T\textsubscript{m} = 363 °C, yet no isotropic transition as the irregularity prohibited the formation of a liquid crystalline morphology.

Figure 5. The effect of alkyl spacer length on the thermal transitions and liquid crystallinity of SDE-containing polyesters.

**Thermomechanical, Tensile, and Rheological Characterization**

DMA afforded the moduli of the polyesters as a function of temperature. Figure 6 shows the DMA and tan delta curves for poly(SDE-HD) and poly(SDE-HD)\textsubscript{90}-co-poly(SDE-BD)\textsubscript{10}. The polymers both exhibited a small drop in the modulus at \textasciitilde70 °C and maintained glassy moduli until the onset of flow, 242 °C and 228 °C for the homopolymer and copolymer respectively. The dimensional stability achieved over the wide temperature range is promising for these polyesters to function as protective coatings and encasings in the weatherable conditions of space travel. Tensile properties yielded another measure of stiffness, a Young’s modulus of 890 ± 150 MPa. An average stress at break of 30 ± 8 MPa and an average strain at break of 4 ± 2 % were also determined. Melt rheology afforded the flow properties of poly(SDE-HD). Figure 7 depicts the result of a 1 Hz frequency sweep at various temperatures. As expected, complex viscosity decreased with increasing temperature and the negative slope of the complex viscosity \textit{vs} frequency curve illustrated the shear thinning of this polymer. Shear thinning is an important property to establish for predicting processability and is characteristic of liquid crystallline polyesters.\textsuperscript{2}
Figure 6. DMA and tan delta curves for poly(SDE-HD) (solid line) and poly(SDE-HD)\textsubscript{90-co-poly(SDE-BD)}\textsubscript{10} (dotted line).

Figure 7. Melt rheology of poly(SDE-HD) at various temperatures.

**Conclusions**

We investigated (co)polyesters comprised of 4,4’-dimethyl-\textit{trans}-stilbene dicarboxylate (SDE), 1,6-hexanediol (HD), and 1,4-butanediol (BD) for use in aerospace applications. The ability to melt press films was indicative of obtaining high molecular weight and zero-shear viscosity comparisons showed an increased molecular weight upon solid-stating. These (co)polyesters demonstrated thermal stability of greater than 360 °C and liquid crystalline morphologies, confirmed using polarized optical microscopy, with melting temperatures ranging from 253 – 196 °C. Dynamic mechanical analysis afforded moduli ~1000 MPa and tensile data resulted in a Young’s modulus of the same magnitude. Melt rheology was also performed and showed the characteristic shear thinning expected of liquid crystalline polyesters. An investigation of alkyl spacer length and composition reinforced the importance of regularity and limited flexibility necessary to maintain a liquid crystalline morphology.

**Acknowledgements**

This material is based upon work supported in part by the Virginia Space Grant Consortium and the U.S. Army Research Laboratory and the U.S. Army Research Office under the Army Materials Center of Excellence Program, contract W911NF-06-2-0014. The authors would also like to thank Eastman Chemical Company for providing the SDE monomer and Solvay for financial support.

**References**


