Effects of Arm Number and Arm Length on Thermal Properties of Linear and Star-shaped Poly(D,L-lactide)

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Abstract: Influences of arm number and arm length of poly(D,L-lactide)’s (PDLLs) on their thermal properties were investigated. The PDLLs with linear (1 arm) and star (4, 6 and 16 arms) shapes were synthesized via ring-opening polymerization of DLL monomer in bulk at 130°C for 24 h under nitrogen atmosphere. Stanton octoate was used as a catalyst. Initiators containing hydroxyl end groups of 1, 4, 6 and 16 were chosen as core molecules for synthesizing 1-, 4-, 6- and 16-armed PDLLs, respectively. Thermal properties of the PDLLs observed from their differential scanning calorimetric and thermogravimetric thermograms strongly depended upon their arm numbers and arm lengths. For the same DLL/initiator ratio (208/1 by mole), glass transition temperatures ($T_g$) and temperatures of maximum decomposition rate ($T_{\Delta_{\text{max}}}$) of the PDLLs decreased when the arm length decreased (or arm number increased). For similar PDLL arm lengths (4, 500 and 4,900 g mol$^{-1}$ for 6-armed star-shaped and 1-armed linear PDLLs, respectively), the $T_g$ and $T_{\Delta_{\text{max}}}$ of star-shaped PDLL was higher than that of the linear PDLL.

Keywords: Polyesters, ring-opening polymerization, differential scanning calorimetry, glass transition temperatures, thermogravimetry, thermal stability

INTRODUCTION

Poly(D,L-lactide) is an important polyester with biodegradability and biocompatibility which have potential applications in biomedical, pharmaceutical and agricultural. Its properties have been tailored by block copolymerization with methoxy poly(ethylene glycol) (MPEG) for use as specific applications such as drug delivery systems (Phromsopa and Baimark, 2009) and nerve guides (Kotsaeng et al., 2009). The glass transition temperature of MPEG-b-PDLL block copolymer was lower than the PDLL. Therefore, MPEG-b-PDLL films showed higher film flexibility than that of the PDLL film. Recently, star-shaped biodegradable polyesters containing 3 molecular arm numbers (or higher) have attracted much attention because of their particular properties resulting from their special three-dimensional structures (Zhao et al., 2002; Odelius and Albertson, 2008). The polyesters with different arm numbers have been synthesized using initiators containing different hydroxyl end groups. The chemical structures in each arm were the same. Influences of arm number and arm length on crystallinity, melting temperature and thermal degradation of these star-shaped polyesters have been widely investigated, especially poly(L-lactide) (Zhao et al., 2002; Danko et al., 2005; Biela et al., 2005; Wang and Dong, 2006; Zhang and Zheng, 2007) and poly(e-caprolactone) (Nunez et al., 2004; Nunez and Gedde, 2005; Meier and Schubert, 2005; Xie and Gan, 2009). However, the structure-property relationship of star-shaped poly(D,L-lactide)’s has been scarcely published (Korhonen et al., 2001; Yuan et al., 2005). Moreover, the thermal properties of star-shaped PDLLs with arm numbers of 1, 4, 6 and 16 have not been compared in each research work.

In the current work, we report the influences of arm number and arm length on thermal properties of PDLLs. The 1-, 4-, 6- and 16-armed PDLLs have been investigated and their structure-thermal property relationships are discussed. Temperatures of thermal transition and decomposition were determined for this purpose. The molecular shapes of PDLLs with arm numbers of 1, 4, 6 and 16 arms are illustrated in Scheme 1a-d. The 1-armed PDLL is a linear PDLL whereas the 4-, 6- and 16-armed PDLL are star-shaped PDLLs. For the PDLLs synthesized with the same monomer/initiator mole ratio, the arm lengths (or molecular weight of each arm) decreased when the arm number increased, as shown in Fig. 1a-d. The 1- and 6-armed PDLLs with similar arm lengths were also compared in their thermal properties.

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Scheme 1: Molecular shapes of PDLLs with different arm number. (a) 1-armed linear PDLL, (b) 4-armed star-shaped PDLL, (c) 6-armed star-shaped PDLL and (d) 16-armed star-shaped PDLL.

Fig. 1: Molecular structures of initiators. (a) 1-dodecanol, (b) Pentaerythritol, (c) Dipentaerythritol and (d) Boltom H2O

MATERIALS AND METHODS

This research was conducted on November 2009-April 2010 at Mahasarakham University, Mahasarakham, Thailand.

Materials: D,L-lactide (DLL) was synthesized by well established procedures from DL-lactic acid (90% Fluka, Switzerland). DLL was purified by repeated re-crystallization from distilled ethyl acetate at least 4 times. The DLL was dried in a vacuum oven at 50°C for 48 h before use. 1-dodecanol (98%, Fluka, Switzerland) was used as an initiator containing one hydroxyl end group and purified by distillation under reduced pressure before being stored over molecular sieves. Pentaerythritol (99%, Aldrich, USA), dipentaerythritol (99%, Aldrich, USA) and Boltom H2O (Perstorp Specialty Chemicals, Sweden) were dried in a vacuum oven for 24 h before use as initiators containing 4-, 6- and 16-hydroxy end groups. Stannous octoate (95% Sigma, USA), Sn(Oct)$_2$, was used without further purification.

Methods

Synthesis of linear and star-shaped poly(D,L-lactide): The poly(D,L-lactide)s (PDLLs) with different arm numbers (1-, 4-, 6- and 16-armed) were polymerized in bulk at 130°C for 24 h under nitrogen atmosphere. DLL/initiator ratios of 208/1 by mole were used. The theoretical molecular weights of PDLLs were approximately 30,000 g mol$^{-1}$, designed as PDLL30,000. Hydroxyl end group compounds and Sn(Oct)$_2$ were used as the initiating system. Sn(Oct)$_2$ concentration was kept constant at 0.02 mol.%. The as-polymerized PDLLs were purified by being dissolved in chloroform before precipitated in cool n-hexane before drying to constant weight in a vacuum oven at room temperature before characterization. Linear PDLL with theoretical molecular weight of 5,000 g mol$^{-1}$, designed as PDLL5,000 was also synthesized for comparison in thermal properties. For PDLL5,000, DLL/initiator ratio and Sn(Oct)$_2$ concentration were 35/1 by mole and 0.02 mol.%, respectively.

Characterization of linear and star-shaped poly(D,L-lactide): The intrinsic viscosity, [η], of PDLLs were determined from flow-time measurements on a diluted series of solutions in chloroform (CHCl$_3$) as solvent at 30°C using viscometrically.

Molecular weight characteristics of the PDLLs were characterized by $^1$H-NMR spectrometry using a Bruker Avance DPX 300 $^1$H-NMR Spectrometer and Gel
Permeation Chromatography (GPC) using a Waters 717 plus Autosampler GPC equipped with an Ultrastyragel® column operating at 40°C and employing universal calibration. 1H-NMR spectra were obtained from copolymer solutions in deuterated chloroform (CDCl₃) using tetramethylsilane as internal reference. For GPC analysis, tetrahydrofuran was used as the solvent at a flow rate of 1 mL min⁻¹.

Thermal properties of the PDLLs was carried out by means of Differential Scanning Calorimetry (DSC) using a Perkin-Elmer DSC Pyris Diamond and thermogravimetry (TG) using a TA-Instrument TG SDT Q600 thermogravimetric analyzer. For DSC analysis, PDLL samples of 5-10 mg in weight were heated at 10°C min⁻¹ under a helium atmosphere in order to observe their glass transition temperatures (Tg) from their second heating scans. For the second heating scans, the PDLLs were first heated to 150°C before fast cooling (quenching) according to the DSC instrument's own default cooling mode before the second run. For TG analysis, 5-10 mg sample was heated from 50 to 1,000°C at the heating rate of 20°C min⁻¹ under nitrogen atmosphere.

RESULTS

The PDLLs with different arm numbers were synthesized using initiators with different numbers of hydroxyl end groups. Molecular structures of the initiators are presented in Fig. 1a-d. The 1-dodecanol, pentaerythritol, dipentaerythritol and Bolton H2O were used for preparing 1-, 4-, 6- and 16-armed PDLLs, respectively. Each hydroxyl end group can ring-opening polymerize the DLL monomer by using stannous octoate as a catalyst, as shown in Fig. 2.

The resulting linear and star-shaped PDLLs can be synthesized via ring-opening polymerization with 88-94% yields. Table 1 reports the intrinsic viscosities ([η]) and molecular weight characteristics of linear and star-shaped PDLLs. For PDLL30,000, the [η] decreased when the arm number increased. The [η] of 1-armed linear PDLL5,000 was lower than that of the 6-armed star-shaped PDLL30,000.

Figure 3 and 4 show 1H-NMR spectra of 1-armed linear and 16-armed star-shaped PDLLs with peak assignments as examples. Number-average molecular weights (Mn) of the PDLLs were calculated based on integral peak areas of their 1H-NMR spectra. From 1H-NMR spectrum in Fig. 3, the ethylene protons (CH2, peak c) of initiator at 3.9-4.2 ppm and the methine protons (CH, peak b) of DLL units at 4.9-5.3 ppm were chosen for the Mn measurement (Korhonen et al., 2001). The Mns of 4- and 6-armed star-shaped PDLLs were also calculated from these integral proton peak areas of their 1H-NMR spectra. Whereas, the overlapped integral peak area (peaks b' + d + d') at 3.9-4.4 ppm and the methine protons (CH, peak b) of DLL units at 4.9-5.3 ppm in 1H-NMR spectrum of 16-armed star-shaped PDLL (Fig. 4) were used for this purpose according to the literature (Zhang and Zheng, 2007).

Fig. 2: Ring-opening polymerization reaction of D,L-lactide

Fig. 3: 1H-NMR spectrum of 1-armed linear PDLL30,000 (peak assignments as shown)
Table 1: Viscosity and molecular weight characteristics of linear and star-shaped PDLLs

<table>
<thead>
<tr>
<th>PDLLs</th>
<th>[n] (DL g⁻¹)</th>
<th>Mₛ,obs (g mol⁻¹)</th>
<th>Mₛ,INT (g mol⁻¹)</th>
<th>Mₛ,GPC (g mol⁻¹)</th>
<th>MWD⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-armed linear PDLL5,000</td>
<td>0.098</td>
<td>4.660</td>
<td>4.900</td>
<td>4.900</td>
<td>1.5</td>
</tr>
<tr>
<td>1-armed linear PDLL30,000</td>
<td>0.524</td>
<td>28.200</td>
<td>29.500</td>
<td>33.139</td>
<td>1.5</td>
</tr>
<tr>
<td>4-armed star-shaped PDLL30,000</td>
<td>0.349</td>
<td>27.300</td>
<td>30.100</td>
<td>29.058</td>
<td>1.4</td>
</tr>
<tr>
<td>6-armed star-shaped PDLL30,000</td>
<td>0.259</td>
<td>27.900</td>
<td>29.800</td>
<td>27.400</td>
<td>1.4</td>
</tr>
<tr>
<td>16-armed star-shaped PDLL30,000</td>
<td>0.115</td>
<td>26.490</td>
<td>30.300</td>
<td>22.115</td>
<td>1.3</td>
</tr>
</tbody>
</table>

*Calculated from theoretical Mₛ, † (yield/100) [theoretical Mₛ was determined from monomer feed ratios]. ‡Calculated from ¹H-NMR spectra. §Obtained from GPC curves; MWD: Molecular weight distribution.

Fig. 4: ¹H-NMR spectrum of 16-armed star-shaped PDLL5,000 (peak assignments as shown)

Number-average molecular weights (Mₛ) of the PDLLs calculated from feed ratios and ¹H-NMR spectra were nearly 30,000 g mol⁻¹. However, the Mₛ of the PDLLs obtained from GPC curves slightly decreased as the arm number increased. Molecular weight distributions of the linear and star-shaped PDLLs showed narrow values in the range of 1.3-1.5 (Table 1). The GPC curves of all PDLLs showed unimodal curves, as example of which is shown in Fig. 5 for the 6-armed star-shaped PDLL30,000.

Thermal transition temperature of the PDLLs was determined by DSC. Figure 6 shows DSC thermograms of the PDLLs. The glass transition temperatures (Tg) obtained from the DSC thermograms are summarized in Table 2. For PDLL30,000, the Tg decreased as the increasing of arm number. While, the Tg of 1-armed linear PDLL5,000 was lower than that of the 6-armed star-shaped PDLL30,000.

Thermal stability of the PDLLs was analyzed by TGA. Figure 7 shows the comparison of %remaining weight of linear and star-shaped PDLLs with different arm numbers from their TG thermograms. The weight loss showed a single stage. The 1-armed linear PDLL30,000

Table 2: Thermal properties of linear and star-shaped PDLLs

<table>
<thead>
<tr>
<th>PDLLs</th>
<th>Arm length (g mol⁻¹)</th>
<th>Tg (°C)</th>
<th>Tg,α (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-armed linear PDLL5,000</td>
<td>4.900</td>
<td>30</td>
<td>272</td>
</tr>
<tr>
<td>1-armed linear PDLL30,000</td>
<td>29.500</td>
<td>43</td>
<td>374</td>
</tr>
<tr>
<td>4-armed star-shaped PDLL30,000</td>
<td>7.525</td>
<td>41</td>
<td>310</td>
</tr>
<tr>
<td>6-armed star-shaped PDLL30,000</td>
<td>4.500</td>
<td>39</td>
<td>302</td>
</tr>
<tr>
<td>16-armed star-shaped PDLL30,000</td>
<td>1.894</td>
<td>36</td>
<td>250</td>
</tr>
</tbody>
</table>

*Calculated from Mₛ, † arm number. ‡Tg,α = Glass transition temperatures obtained from DSC thermograms, Tg,α = Temperatures of maximum decomposition rate obtained from DTG thermograms.

Fig. 5: GPC curve of 6-armed star-shaped PDLL30,000

Fig. 6: Second heating scan DSC thermograms of (a) 1-armed PDLL5,000, (b) 1-armed PDLL30,000, (c) 4-armed PDLL30,000, (d) 6-armed PDLL30,000 and (e) 16-armed PDLL30,000

and PDLL5,000 exhibited the slowest and the fastest thermal decomposition, respectively. The thermal decomposition of PDLLs with higher arm number was faster than those of lower arm numbers.
The thermal decomposition of the PDLLs can be clearly observed from differential TG (DTG) thermograms, as shown in Fig. 8. From DTG thermograms, the temperature of maximum decomposition rate \( T_{\text{d,max}} \) can be determined and is reported in Table 2. It was found that all PDLLs had a single \( T_{\text{d,max}} \). For PDLL30,000, the \( T_{\text{d,max}} \) values decreased when the arm number increased. The \( T_{\text{d,max}} \) of 1-arm linear PDLL5,000 showed lower than those of the PDLL30,000s.

**DISCUSSION**

The initiators with hydroxyl end groups of 1, 4, 6 and 16 groups (Fig. 1) were used for synthesizing the 1-, 4-, 6- and 16-arm PDLLs, respectively. The DLL/initiator mole ratio of 208/1 was used to prepare the PDLL with theoretical molecular weight approximately 30,000 g mol\(^{-1}\) (PDLL30,000). Therefore, the arm numbers and the arm lengths of each PDLL30,000 are difference, as reported in Table 2. When the DLL/initiator mole ratio (or molecular weight) was kept constant, the arm lengths decreased as the arm number increased.

The \([\eta]\) of PDLL solution directly related to hydrodynamic volume of each PDLL molecule in PDLL solution. The higher arm number polyesters showed smaller hydrodynamic volume (Wang and Dong, 2006). Therefore, the decreasing \([\eta]\) values of PDLL30,000 solutions as the increasing of arm number (see Table 1). The results can be explained as following. The hydrodynamic volume of PDLL molecules in PDLL solution decreased as the arm number increased (or the arm length decreased). Then, the higher arm number PDLL induced lower the \([\eta]\) value.

The actual \( M_\text{w} \) values of the PDLLs obtained from their %yields and \(^1\)H-NMR spectra are similar to the theoretical \( M_\text{w} \) values (Table 1). Then, these similar molecular weight PDLLs with different arm numbers (e.g., 1-, 4-, 6- and 16-arm PDLL30,000s) were compared for their thermal properties, \( T_\text{g} \) and \( T_{\text{d,max}} \) values. The effect of molecular shapes (1-arm linear PDLL5,000 and 6-arm star-shaped PDLL30,000) on their thermal properties of PDLLs was also determined. The 1-arm PDLL5,000 will be used to compare its thermal properties with the 6-arm star-shaped PDLL30,000. Because of each PDLL arm length of the 6-arm star-shaped PDLL30,000 was approximately 5,000 g mol\(^{-1}\).

From Table 2, it was found that the \( T_\text{g} \) of the PDLL30,000 slightly decreased with the arm length (or arm number increased) according to the literature (Korhonen et al., 2001; Wang and Dong, 2006; Zhang and Zheng, 2007). This may be proposed that the PDLL30,000 with shorter arm length can easier rotate than the longer arm length during glass transitional state. This indicated that the \( T_\text{g} \) of PDLLs can be controlled from their PDLL molecular shapes (or arm numbers). The \( T_\text{g} \) of PDLL have been adjusted by random (Baimar et al., 2010) and block (Baimar et al., 2007) copolymerization. Therefore, star-shaped polymerization is an alternative method for adjusting the \( T_\text{g} \) of PDLL. However, each PDLL arm may difficult to rotate when it connected to other PDLL arms in the star-shaped PDLLs. This induces higher \( T_\text{g} \) value. This effect was confirmed by comparison \( T_\text{g} \) of the 1-arm linear PDLL5,000 (30°C) and the 6-arm star-shaped PDLL30,000 (30°C), as reported in Table 2. Although, each arm length in the 6-arm star-shaped PDLL30,000 was similar to the 1-arm linear PDLL5,000. The \( T_\text{g} \) of the 6-arm PDLL showed higher than the 1-arm PDLL.
The thermal stability of PDLLs can be observed from their TG and DTG curves, as shown in Fig. 7. The difference of their weight loss suggested that these PDLLs exhibited different thermal decomposition profiles, although their molecular weights were almost same for the 1-, 4-, 6- and 16-armed PDLL30,000s. From TG thermograms in Fig. 7, it can be seen that the thermal stability of linear PDLL30,000 was higher than those of the star-shaped PDLL30,000s. The weight losses of star-shaped PDLL30,000s increased with the arm number. This can be explained that the shorter PDLL arms in star-shaped PDLLs were faster thermal degraded than the longer PDLL arm length in linear PDLL (Yuan et al., 2005; Xie and Gan, 2009). The attachment of PDLL arms in star-shaped molecules (Fig. 7d) enhanced thermal stability to compare with the 1-armed linear PDLL5,000 (Fig. 7a). The peaks of DTG thermograms (Fig. 8) are T_{d, max} values. Each PDLLs showed a single T_{d, max} according to a single thermal decomposition stage in TG thermograms. Thermal stability of the PDLLs can be clearly compared from their T_{d, max} values, as summarized in Table 2. The T_{d, max} values of PDLLs decreased with the PDLL arm length (increasing of the arm number). In addition, the T_{d, max} value of PDLL also increased when the PDLL arms were connected to other PDLL arms in star-shaped PDLL. This was compared between 1-armed linear PDLL5,000 and 6-armed star-shaped PDLL30,000.

CONCLUSIONS

The well-defined linear and star-shaped PDLLs with different arm numbers and arm lengths were successfully synthesized. Their molecular weight characteristics were analyzed from viscometric, H-NMR and GPC techniques. From GPC curves, the MWD of all PDLLs exhibited unimodal types. The intrinsic viscosity and M_w values depended upon their arm numbers. The arm lengths of PDLL decreased when the arm number increased. The T_g and T_{d, max} values decreased with the PDLL arm length. For similar arm lengths, the T_g and T_{d, max} values increased when the linear PDLL arms were connected to other PDLL arms to form as star-shaped PDLL.

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