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Biodegradable Linear/Star-shaped Poly(L-lactide) Blends Prepared by Single Step Ring-opening Polymerization

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Abstract: Poly(L-lactide) (PLL) is an environmentally friendly polymer that has widely been used in medical and packaging applications because of its biodegradability and biocompatibility. Star-shaped PLLs are expected to exhibit different properties compared to the linear PLL. The objective of this study was to investigate the effects of blend ratios and blending techniques including single step ring-opening polymerization and solution blending on the characteristics of linear (1-arm)/star-shaped (6-arm) PLL blends. A 1-dodecanol/dipentaerythritol mixture and stannous octoate were used as an initiating system. Intrinsic viscosity, glass transition temperature and crystallizing temperature of the PLL blends steadily increased, while heat of crystallization and heat of melting significantly decreased when the star-shaped blend ratio was increased. However, melting temperature and thermal decomposition did not change. Mechanical properties of the PLL films were also influenced by the blend ratio. The physical and mechanical properties of the PLL blends obtained from single step polymerization depend upon the blend ratio, similar as when they are obtained from the solution blending method.

Key words: Biodegradable polymers, polymer blends, solution blending, thermal properties, mechanical properties

INTRODUCTION

Biodegradable polyesters have attracted much interest in medical and packaging applications because of their biodegradability and biocompatibility (Lim *et al.*, 2008; Gupta *et al.*, 2010; Rudra *et al.*, 2011; Dash and Konkimalla, 2012). Star-shaped biodegradable polyesters contained three or more linear arms radiating from the molecular center. The star-shaped poly(L-lactide) (Wang and Dong, 2006; Zhang and Zheng, 2007), poly(D, L-lactide) (Korhonen *et al.*, 2001; Srisa-ard and Baimark, 2010) and poly(ϵ -caprolactone) (Yuan *et al.*, 2005; Xie and Gan, 2009) have been synthesized and characterized. The viscosity, thermal and mechanical properties and degradation profiles of the star-shaped polyesters were different from conventional linear polyesters (Odelius and Albertson, 2008; Baimark, 2012). The initiators containing three or more hydroxyl end-groups have been used in the preparation of star-shaped polyesters. The properties of star-shaped polyesters such as crystallinity, glass transition temperature, melting temperature and thermal degradation depended upon their arm number and arm length.

Physical blending of polymers is an alternative method that has been widely used to adjust the properties of biodegradable polymers (Hoidy *et al.*, 2010; Srihanam, 2011; Prasong, 2011). Thus, unique properties of polymer blends, quite different from the origin polymers, were obtained. Synthetic polymers were usually melt blended after synthesis. Processing cost, time and thermal degradation during melt blending may be reduced, if the synthetic polymer blends can be prepared through a single step polymerization.

In the current study, the influences of blending method (solution blending and single step ring-opening polymerization) and blend ratio on characteristics of linear/star-shaped PLL blends were determined. The linear/star-shaped PLL blends with blend ratios of 4/1, 2/1, 1/1 and 1/2 w/w were investigated and compared to linear and star-shaped PLLs. The intrinsic viscosity, thermal transition, thermal decomposition and mechanical properties were measured.

MATERIALS AND METHODS

This research was conducted from June 2011- March 2012 at Mahasarakham University, Mahasarakham, Thailand.

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Materials: L-lactide (LL) monomer was synthesized using well-established procedures from L-lactic acid (88% Purac, Thailand). The LL was purified by repeated recrystallization from distilled ethyl acetate and dried in a vacuum oven at 50°C for 48 h before use. 1-dodecanol (98%, Fluka, Switzerland) containing one hydroxyl end group was purified by distillation under reduced pressure before being stored over molecular sieves. It was used as an initiator for preparing 1-arm or linear PLL. Dipentaerythritol (99%, Aldrich, USA) was dried in a vacuum oven at 50°C for 48 h before use as the initiators contained 6-hydroxyl end groups for preparing 6-arm or star-shaped PLL. Stannous octoate (95% Sigma, USA), Sn(Oct)₂, was used without further purification. All reagents used were analytical grade.

Synthesis of linear/star-shaped PLL blends: Linear/star-shaped PLL blends were synthesized by single step ring-opening polymerization, in bulk, at 140°C for 24 h under a nitrogen atmosphere. The theoretical molecular weight of each PLL arm for both linear and star-shaped PLLs was approximately 40,000 g mol⁻¹. The PLL blends were synthesized using the 1-dodecanol/dipentaerythritol mixture and Sn(Oct)₂ as the initiating system. The 1-dodecanol/dipentaerythritol ratios of 24/1, 12/1, 6/1 and

3/1 by mole were used to prepare linear/star-shaped PLL blend ratios of 4/1, 2/1, 1/1 and 1/2 w/w, respectively. These PLL blends were called “polymerized PLL blends”.

The polymerization reaction of the PLL blends is illustrated in Fig. 1. Sn(Oct)₂ concentration was kept constant at 0.01 mol%. As-polymerized PLL blends were purified by being dissolved in chloroform and precipitated in cool n-hexane before drying to a constant weight in a vacuum oven at 50°C. Yield of PLL was calculated based on weight of PLL before and after purification.

The linear and star-shaped PLLs with a theoretical molecular weight of 40,000 g mol⁻¹ in each PLL arm were synthesized. The PLL blends were also prepared by solution blending for comparison. The linear and star-shaped PLL mixture was dissolved in chloroform before drying at room temperature for 24 h and kept in a vacuum oven at room temperature for a week. These PLL blends were called “solution PLL blends”.

Characterization of linear/star-shaped PLL blends:

Intrinsic viscosity, [η], of PLL blends was determined from flow-time measurements on a diluted series of solutions in chloroform (CHCl₃), as the solvent, at 25°C using viscometrically.

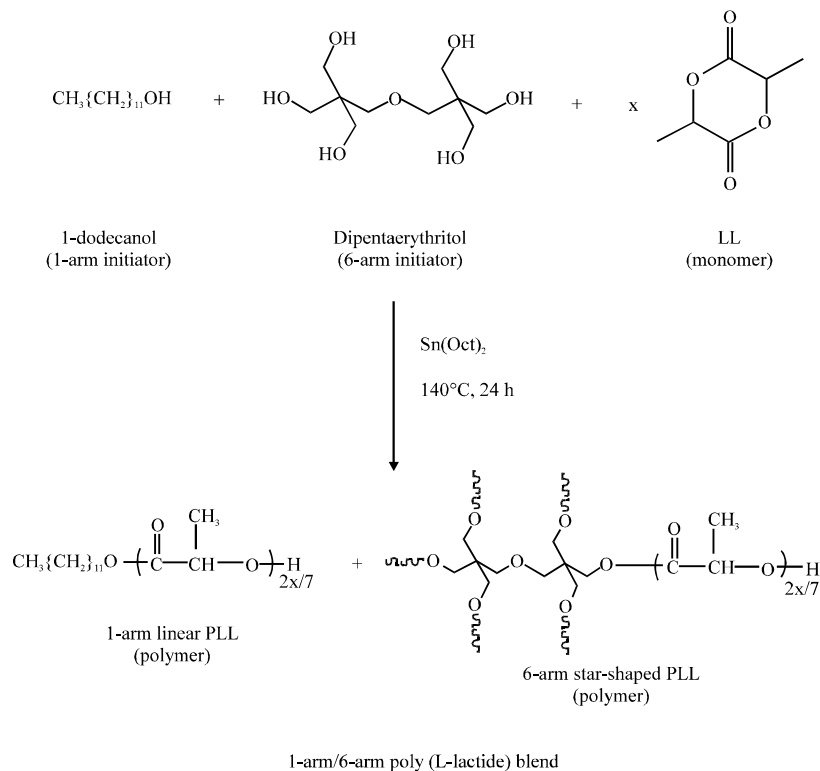


Fig. 1: Single step ring-opening polymerization reaction of linear/star-shaped PLL blends

Thermal transition properties of the PLL blends were determined by means of Differential Scanning Calorimetry (DSC) using a PerkinElmer DSC Pyris Diamond. For DSC analysis, 5-10 mg PLL blend was heated from 20 to 200°C at a rate of 10°C min⁻¹ under a helium flow after quenching from 200 to 0°C in order to observe its glass transition temperature (T_g), crystallizing temperature (T_c), heat of crystallization (ΔH_c), melting temperature (T_m) and heat of melting (ΔH_m).

Thermal decomposition behaviors of the PLL blends were characterized by non-isothermal Thermogravimetric (TG) analysis using a TA-Instrument SDT Q600 TG analyzer. For TG analysis, a sample (~5 mg) was heated from 50 to 600 °C at a rate of 20°C min⁻¹ under a nitrogen atmosphere.

Mechanical properties including stress at break, elongation at break and initial Young's modulus of PLL blend films were measured by tensile testing using a Lloyds LRX+ Universal Mechanical Testing Machine. The films (50 ×15 mm) were performed at 25°C and 65% relative humidity with the speed of 10 mm min⁻¹ and 1 kN load cell. The experimental values for mechanical properties represent averages of measurements from five replicate films.

RESULTS

Yields of linear, star-shaped and polymerized PLL blends measured from the precipitation method were higher than 95%, as would be expected since the polymerizations proceed to near-quantitative conversion. The solution and polymerized PLL blends with different linear/star-shaped PLL blend ratios were obtained by solution blending and single step polymerization, respectively. The initiator mixture (1-dodecanol/dipentaerythritol mixture) was used to prepare the polymerized PLL blends. The blend ratio could be adjusted by varying the 1-dodecanol/dipentaerythritol ratio.

Intrinsic viscosity: Molecular weight characterization was carried out by means of dilute-solution viscometry, as shown in Fig. 2 for both the solution and polymerized PLL blends. It was found that the $[\eta]$ of the linear PLL is lower than that of star-shaped PLL. The effect of blend ratio significantly influenced the $[\eta]$ of the PLL blends, compared with linear and star-shaped PLLs. The $[\eta]$ of PLL blends increased with the star-shaped PLL blend ratio. The $[\eta]$ changes for the solution and polymerized PLL blends for the same linear/star-shaped PLL blend ratio showed similar evidence.

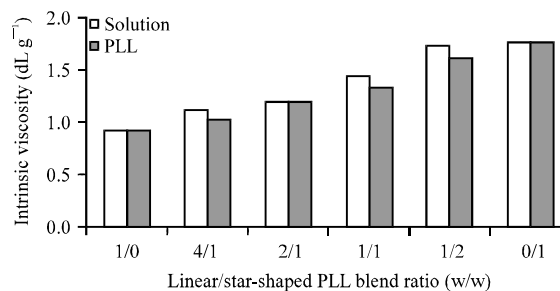


Fig. 2: Intrinsic viscosity of solution and polymerized PLL blends with different linear/star-shaped PLL blend ratios

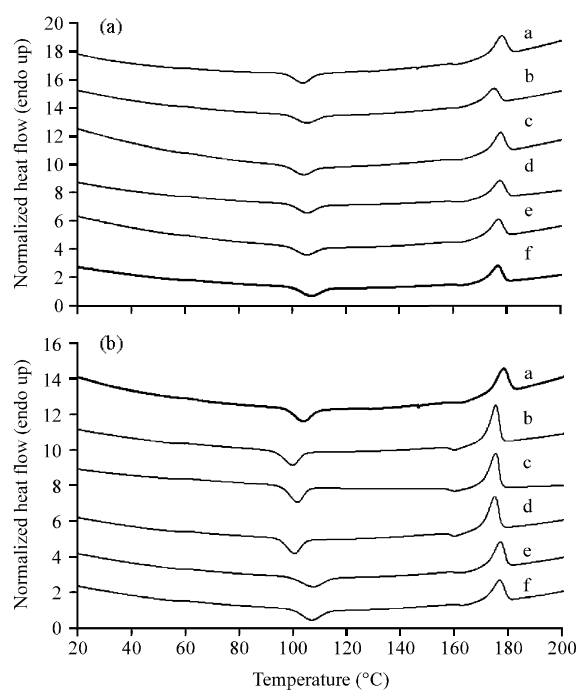


Fig. 3(a-b): Second heating scan of DSC thermograms for (a) Solution and (b) Polymerized PLL blends with linear/star-shaped PLL blend ratios of a: 1/0, b: 4/1, c: 2/1, d: 1/1, e: 1/2 and f: 0/1 w/w

Thermal transition: Thermal transition properties such as glass transition temperature (T_g), crystallizing temperature (T_c), heat of crystallization (ΔH_c), melting temperature (T_m) and heat of melting (ΔH_m) of the PLL samples were determined from DSC thermograms as shown in Fig. 3. The DSC results are summarized and compared in Fig. 4 and 5. It can be seen that the T_g and T_c of the linear PLL were lower and the Δh_c and Δh_m were higher than the star-shaped PLL. The T_g and T_c of the PLL blends increased while the ΔH_c and ΔH_m decreased as the

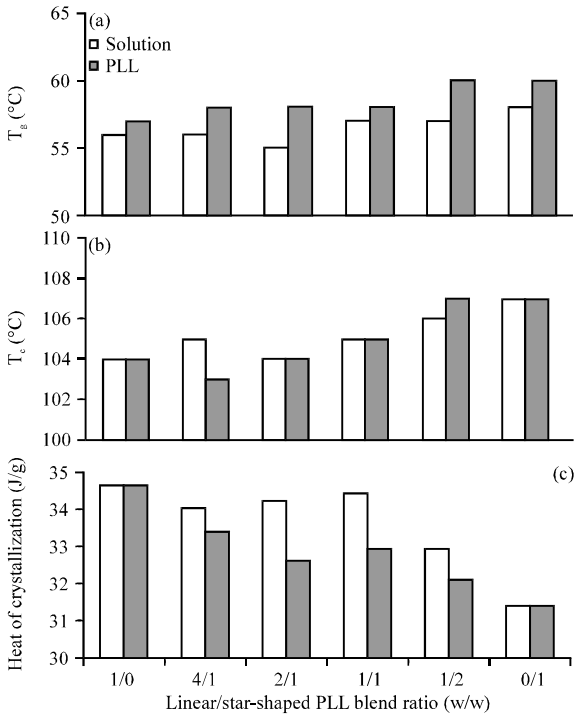


Fig. 4(a-c): (a) T_g , (b) T_c and (c) Heat of crystallization of solution and polymerized PLL blends

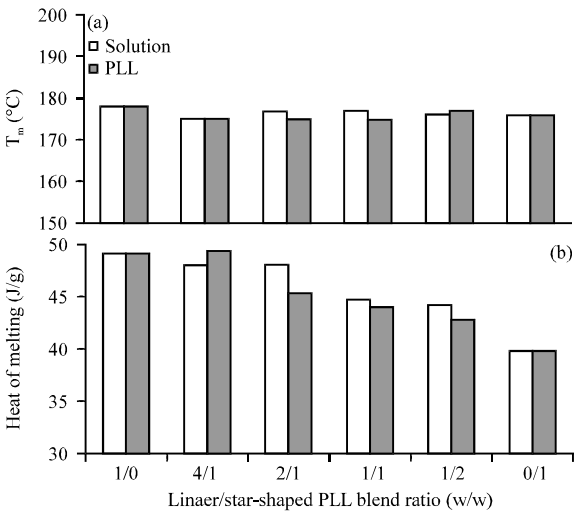


Fig. 5(a-b): (a) T_m and (b) Heat of melting of solution and polymerized PLL blends

star-shaped PLL blend ratio increased. However, the T_m of the linear, star-shaped and PLL blends are similar in the range of 175-178°C.

Thermal decomposition: The thermal decomposition of the PLL samples was studied from the TG thermograms, as

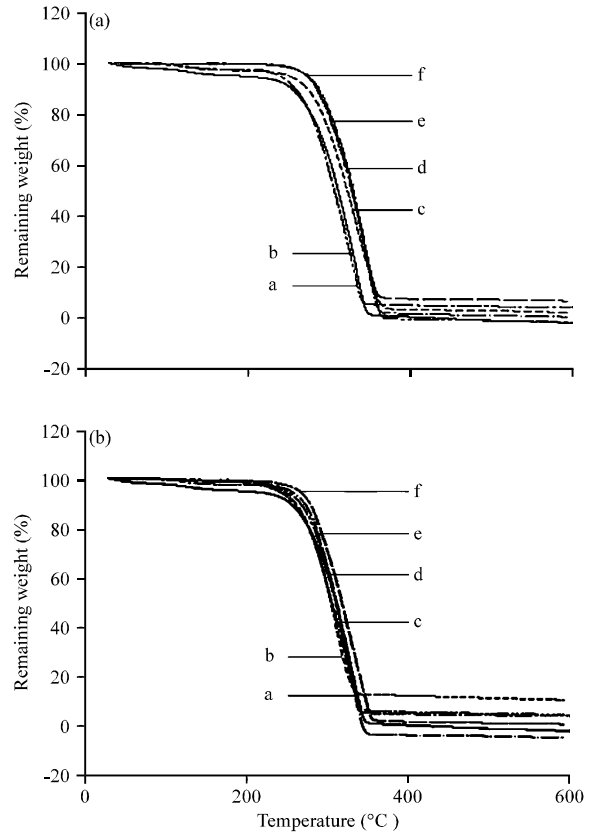


Fig. 6(a-b): TG thermograms of (a) Solution and (b) Polymerized PLL blends with linear/star-shaped PLL blend ratios of a: 1/0, b: 4/1, c: 2/1, d: 1/1, e: 1/2 and f: 0/1 w/w

illustrated in Fig. 6. The linear PLL, star-shaped PLL, solution PLL blends and polymerized PLL blends comprised of a single decomposition step in the range of 200-400°C. The differential TG (DTG) thermograms in Fig. 7 clearly provide evidence for a single-step decomposition process for all PLL samples. The decomposition peaks are also in the range of 200-400°C according to the TG thermograms in Fig. 6. The TG and DTG results indicated that the thermal decomposition behaviors of solution and polymerized PLL blends in all blend ratios are similar to the linear and star-shaped PLL.

Mechanical properties: All the PLL film thicknesses are in the range 35-40 μm . Figure 8 shows the results of the mechanical properties of PLL films. Tensile stress at break, tensile strain at break and initial Young's modulus for the linear PLL film were lower than the star-shaped PLL film. The mechanical properties of the solution PLL blend films

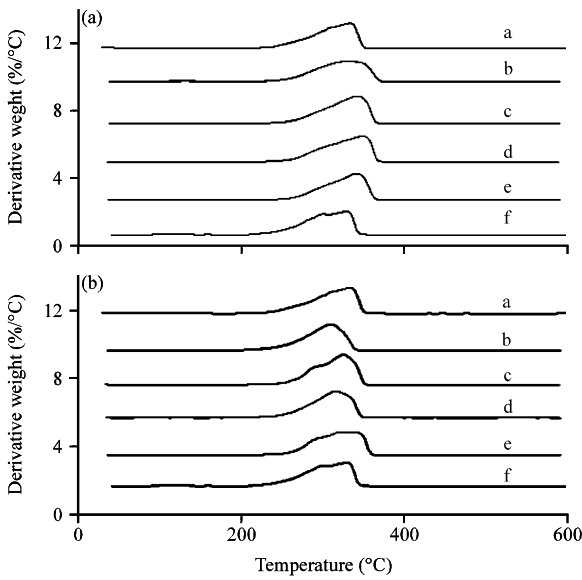


Fig. 7(a-b): TG thermograms of (a) Solution and (b) Polymerized PLL blends with linear/star-shaped PLL blend ratios of a: 1/0, b: 4/1, c: 2/1, d: 1/1, e: 1/2 and f: 0/1 w/w

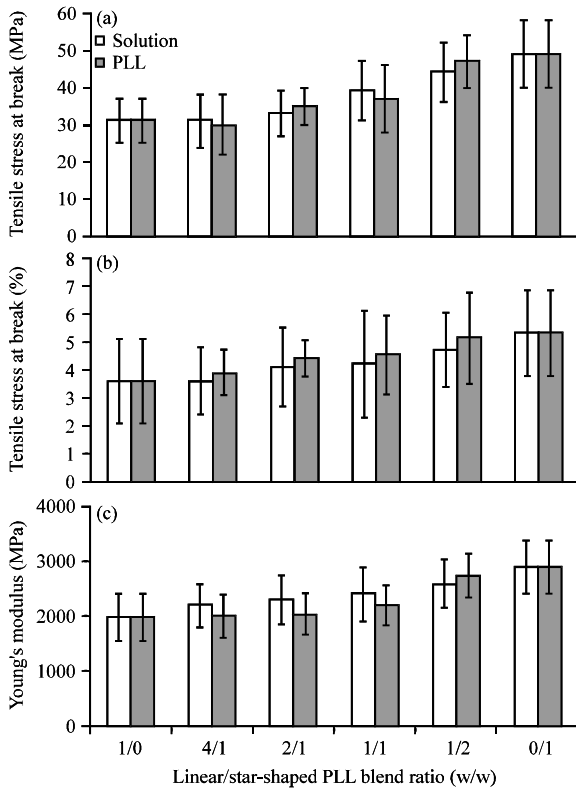


Fig. 8(a-c): Tensile properties of PLL blend films with different linear/star-shaped PLL blend ratios of solution and polymerized PLL blends. Bars represent SD

slightly increased with increasing star-shaped PLL blend ratio similar to the polymerized PLL blend films for the same blend ratio.

DISCUSSION

The 1-dodecanol and dipentaerythritol initiators containing 1 and 6 hydroxyl end-groups, respectively, have been used to synthesis the 1-arm linear PLL and the 6-arm star-shaped PLL, respectively (Srisa-ard and Baimark, 2010). In this research, a mixture of 1-dodecanol and dipentaerythritol was used to polymerize linear and star-shaped PLLs in the same reaction flask. The linear/star-shaped PLL blends were then obtained. It could be expected that the linear/star-shaped PLL blend ratio can be adjusted by varying the 1-dodecanol/dipentaerythritol ratio. The potential for single step ring-opening polymerization and solution blending for preparing the PLL blends was determined and compared.

Intrinsic viscosity: It could be estimated that the reactivity of the hydroxyl end-groups of both 1-dodecanol and dipentaerythritol initiators are similar. Each arm length (molecular weight) of the linear and star-shaped PLLs was nearly the same value. The six arm attachment of the star-shaped PLL gave larger hydrodynamic volume and higher $[\eta]$ than the linear PLL. The 6-armed star-shaped poly(D,L-lactide) showed higher $[\eta]$ than the linear PLL for the same arm length ($5,000 \text{ g mol}^{-1}$) as reported in previous work (Srisa-ard and Baimark, 2010). For both the solution and polymerized PLL blends, the $[\eta]$ increased as the star-shaped PLL blend ratio increased due to the higher $[\eta]$ of the star-shaped PLL. This suggests that the $[\eta]$ of the PLL blends was controlled by blend ratio. The viscosity results showed that the 1-dodecanol/dipentaerythritol mixture used is effective producing the PLL blends with different $[\eta]$ through the single step ring-opening polymerization.

Thermal transition: From DSC thermograms in Fig. 3, the solution and polymerized PLL blends in all blend ratios are semi-crystalline. A melting point was observed. The T_g of the linear PLL was lower than the star-shaped PLL Fig. 4a due to smaller molecules of linear PLL. The smaller PLL molecule can more easily rotate than the larger PLL molecule during the glass transitional state (Srisa-ard and Baimark, 2010). Each PLL arm may be difficult to rotate when it is attached to other PLL arms to form the star-shaped PLL. This induced a higher T_g . The T_g of star-shaped PLL strongly depended upon their arm number and arm length (Korhonen *et al.*, 2001). It can be seen that

the T_g s of the solution and polymerized PLL blends slightly increased as the star-shaped PLL blend ratio increased. This is due to the higher T_g of the star-shaped PLL than the linear PLL.

The PLL crystallization gave an exothermic peak of T_c . The T_c of linear PLL was lower than the star-shaped PLL. The T_c of the blend PLL increased with the star-shaped PLL blend ratio. This may be explained due to the larger molecule of the star-shaped PLL. Each PLL arm may be difficult to rearrange for crystallization when it is attached to other PLL arms to form the star-shaped PLL. This induced a higher T_c . Due to the higher T_c of the star-shaped PLL, the T_c of PLL blends increased with the star-shaped PLL blend ratio. The Δh_c , Fig. 4c and ΔH_m , Fig. 5b of the PLL blends decreased as the star-shaped PLL blend ratio increased because the star-shaped PLL exhibited lower ΔH_c and ΔH_m than the linear PLL. The attachment of PLL arms may inhibit crystallization. The thermal transition results indicated that the T_g , T_c , ΔH_c and ΔH_m of the PLL blends were controlled from the blend ratio. Therefore, single step polymerization of linear/star-shaped PLL blends is an alternative technique for adjusting thermal transition properties of PLL blends.

Thermal decomposition: From the TG and DTG thermograms in Fig. 6 and 7, respectively, the thermal decompositions of all the PLL blends were shown to be similar. The similar melting temperature Fig. 5a and thermal decomposition behaviors suggested that the processing window of these linear PLL, star-shaped PLL and PLL blends are not different. The various blend ratios of linear/star-shaped PLL do not affect their processing temperature. Usually, thermal stability of star-shaped polyesters directly related to their molecular weights (Yuan *et al.*, 2005). The lower molecular weight polyester induced poor thermal stability. However, the thermal stabilities of high molecular weight polyesters were similar. The all PLL blends in this work exhibited the high $[\eta]$ values (>0.9 dL g⁻¹) suggested they were high molecular weight PLLs. Thus the thermal stabilities of linear/star-shaped PLL blends with different blend ratios were similar.

Mechanical properties: The mechanical properties of polymer strongly depended upon the polymer molecular weight (Lim *et al.*, 2008). The $[\eta]$ is directly related to polymer molecular weight. The mechanical properties including tensile stress at break, tensile strain at break and Young's modulus of the PLL blend films increased when the $[\eta]$ of PLL blend was increased. Present results proved that the mechanical properties of PLL blend films could be also controlled with the blend ratio.

CONCLUSION

In the present study, linear/star-shaped PLL blends with various blend ratios were successfully prepared by single step ring-opening polymerization. For the same blend ratio, the characteristics of PLL blends obtained from single step polymerization and solution blending were similar. Their characteristics including intrinsic viscosity, thermal transition properties and mechanical properties depend upon the linear/star-shaped PLL blend ratio. These PLL blends are considered as promising biodegradable materials for biomedical and packaging applications. Research on *in vitro* biodegradation of these PLL blends is under investigation.

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