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

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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. Stannous 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 ($T_{d,max}$) 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 $T_{d,max}$ of star-shaped PDLL was higher than that of the linear PDLL.

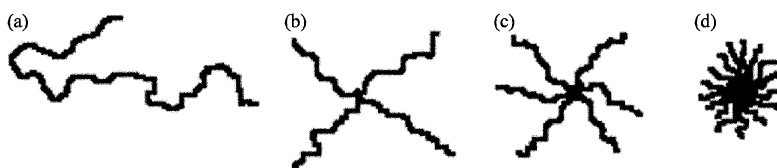
Key words: Polyesters, ring-opening polymerization, differential scanning calorimetry, glass transition temperatures, thermogravimetry, thermal stability

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 (Phromospha and Baimark, 2009) and nerve guides (Kotseang *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(ϵ -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.



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

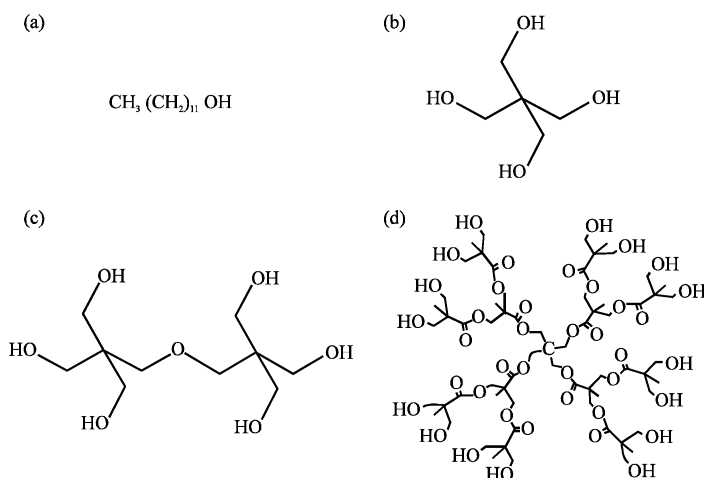


Fig. 1: Molecular structures of initiators. (a) 1-dodecanol, (b) Pentaerythritol, (c) Dipentaerythritol and (d) Boltom H20

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 Boltorn H20 (Perstorp Specialty Chemicals, Sweden) were dried in a vacuum oven for 24 h before use as initiators containing 4-, 6- and 16-hydroxyl 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)s: 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)s: The intrinsic viscosity, [η], of PDLLs were determined from flow-time measurements on a diluted series of solutions in chloroform (CHCl₃) as solvent at 30°C using viscometrically.

Molecular weight characteristics of the PDLLs were characterized by ¹H-NMR spectrometry using a Bruker Avance DPX 300 ¹H-NMR Spectrometer and Gel

Permeation Chromatography (GPC) using a Waters 717 plus Autosampler GPC equipped with an Ultrastaygel® 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 (T_g) 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-dodeccanol, pentaerythritol, dipentaerythritol and Boltorn H20 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-arm linear and 16-armed star-shaped PDLLs with peak assignments as examples. Number-average molecular weights (M_n) 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

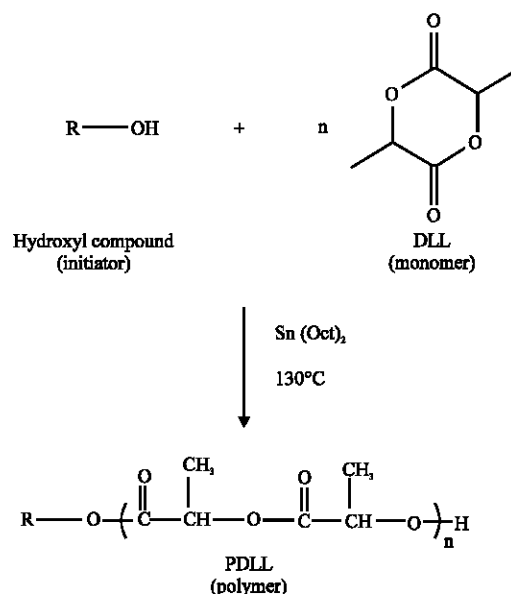


Fig. 2: Ring-opening polymerization reaction of D,L-lactide

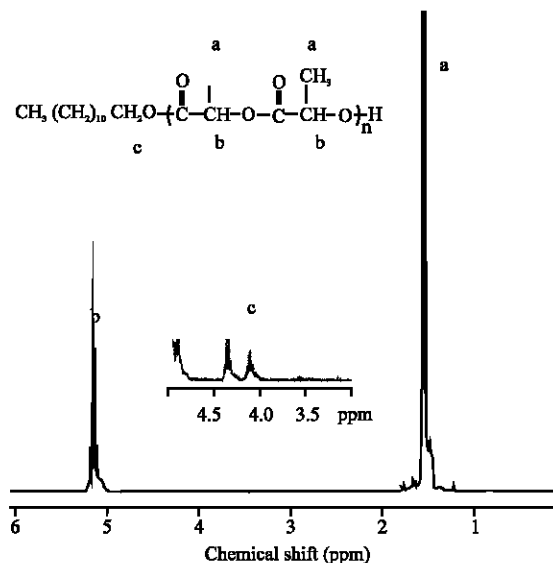


Fig. 3: ¹H-NMR spectrum of 1-armed linear PDLL30,000 (peak assignments as shown)

the M_n measurement (Korhonen *et al.*, 2001). The M_ns 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).

Table 1: Viscosity and molecular weight characteristics of linear and star-shaped PDLLs

PDLLs	$[\eta]$ (dL g ⁻¹)	$M_{n, \text{theor}}^a$ (g mol ⁻¹)	$M_{n, \text{NMR}}^b$ (g mol ⁻¹)	$M_{n, \text{GPC}}^c$ (g mol ⁻¹)	MWD ^c
1-armed linear PDLL5,000	0.098	4.600	4.900	4.900	1.5
1-armed linear PDLL30,000	0.524	28.200	29.500	33.139	1.5
4-armed star-shaped PDLL30,000	0.349	27.300	30.100	29.058	1.4
6-armed star-shaped PDLL30,000	0.259	27.900	29.800	27.400	1.4
16-armed star-shaped PDLL30,000	0.115	26.400	30.300	22.115	1.3

^aCalculated from theoretical $M_n \times (\% \text{yield}/100)$ [theoretical M_n was determined from monomer feed ratios]. ^bCalculated from ¹H-NMR spectra. ^cObtained from GPC curves; MWD: Molecular weight distribution

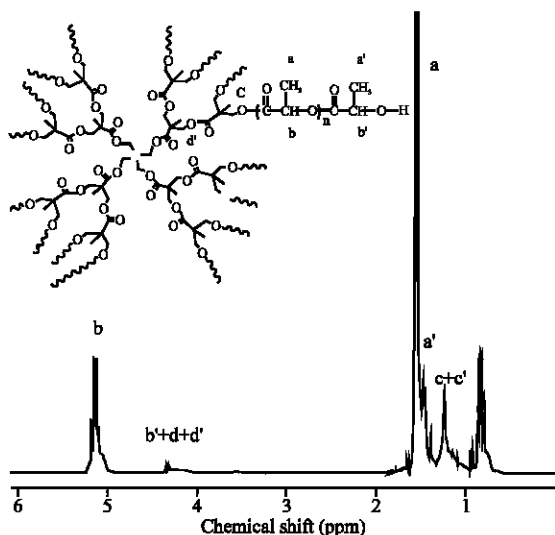


Fig. 4: ¹H-NMR spectrum of 16-armed star-shaped PDLL30,000 (peak assignments as shown)

Number-average molecular weights (M_n) of the PDLLs calculated from feed ratios and ¹H-NMR spectra were nearly 30,000 g mol⁻¹. However, the M_n 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 the 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 (T_g s) obtained from the DSC thermograms are summarized in Table 2. For PDLL30,000, the T_g s decreased as the increasing of arm number. While, the T_g 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

PDLLs	Arm length ^b (g mol ⁻¹)	T_g^b (°C)	$T_{d, \text{max}}^c$ (°C)
1-armed linear PDLL5,000	4.900	30	272
1-armed linear PDLL30,000	29.500	43	374
4-armed star-shaped PDLL30,000	7.525	41	310
6-armed star-shaped PDLL30,000	4.500	39	302
16-armed star-shaped PDLL30,000	1.894	36	290

^aCalculated from $M_{n, \text{NMR}}/\text{arm number}$. ^b T_g = Glass transition temperatures obtained from DSC thermograms, ^c $T_{d, \text{max}}$ = Temperatures of maximum decomposition rate obtained from DTG thermograms

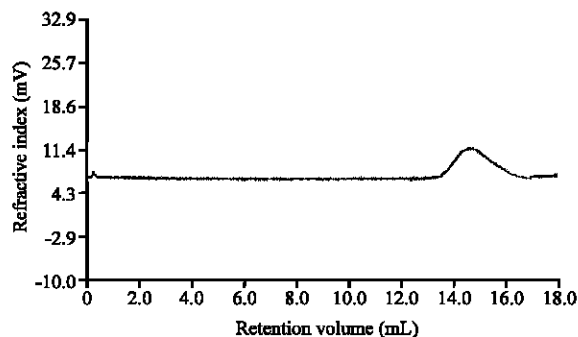


Fig. 5: GPC curve of 6-armed star-shaped PDLL30,000

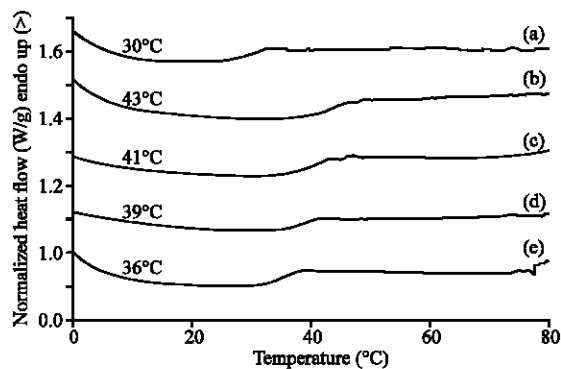


Fig. 6: Second heating scan DSC thermograms of (a) 1-armed PDLL5,000, (b) 1-armed PDLL30,000, (c) 4-armed PDLL30,000, (d) 6-armed PDLL30,000 and (e) 16-armed PDLL30,000

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.

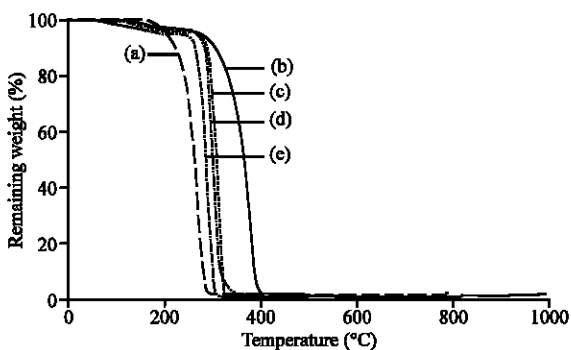


Fig. 7: TG thermograms of (a) 1-armed PDLL5,000, (b) 1-armed PDLL30,000, (c) 4-armed PDLL30,000, (d) 6-armed PDLL30,000 and (e) 16-armed PDLL30,000

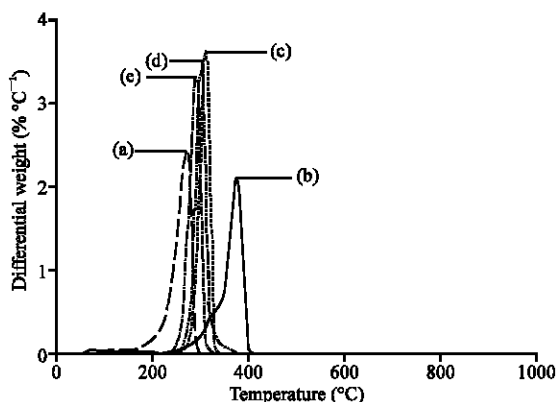


Fig. 8: DTG thermograms of (a) 1-armed PDLL5,000, (b) 1-armed PDLL30,000, (c) 4-armed PDLL30,000, (d) 6-armed PDLL30,000 and (e) 16-armed PDLL30,000

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 ($T_{d,max}$) can be determined and is reported in Table 2. It was found that the all PDLLs had a single $T_{d,max}$. For PDLL30,000, the $T_{d,max}$ values decreased when the arm number increased. The $T_{d,max}$ of 1-armed 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-armed PDLLs, respectively. The DLL/initiator mole ratio of 208/1 was used to prepare the PDLL with

theoretical molecular weight approximately $30,000 \text{ g mol}^{-1}$ (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_n values of the PDLLs obtained from their %yields and $^1\text{H-NMR}$ spectra are similar to the theoretical M_n values (Table 1). Then, these similar molecular weight PDLLs with different arm numbers (e.g., 1-, 4-, 6- and 16-armed PDLL30,000s) were compared for their thermal properties, T_g and $T_{d,max}$ values. The effect of molecular shapes (1-armed linear PDLL5,000 and 6-armed star-shaped PDLL30,000) on their thermal properties of PDLLs was also determined. The 1-armed PDLL5,000 will be used to compare its thermal properties with the 6-armed star-shaped PDLL30,000. Because of each PDLL arm length of the 6-armed star-shaped PDLL30,000 was approximately $5,000 \text{ g mol}^{-1}$.

From Table 2, it was found that the T_g s 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_g s of PDLLs can be controlled from their PDLL molecular shapes (or arm numbers). The T_g of PDLL have been adjusted by random (Baimark *et al.*, 2010) and block (Baimark *et al.*, 2007) copolymerization. Therefore, star-shaped polymerization is an alternative method for adjusting the T_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_g value. This effect was confirmed by comparison T_g s of the 1-armed linear PDLL5,000 (30°C) and the 6-armed star-shaped PDLL30,000 (39°C), as reported in Table 2. Although, each arm length in the 6-armed star-shaped PDLL30,000 was similar to the 1-armed linear PDLL5,000. The T_g of the 6-armed PDLL showed higher than the 1-armed 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, $^1\text{H-NMR}$ and GPC techniques. From GPC curves, the MWD of all PDLLs exhibited unimodal types. The intrinsic viscosity and $M_{n, \text{GPC}}$ 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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