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Synthesis and thermal properties of novel star-shaped poly(L-lactide)s with starburst PAMAM–OH dendrimer macroinitiator

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Abstract

The starburst PAMAM–OH dendrimer (generation 3) as macroinitiator for the synthesis of star-shaped polylactides in the presence of stannous octoate was investigated. Effects of molar ratios of monomer to initiator, monomer to catalyst, monomer conversion, and reaction temperature on polymerization were studied. It is found that 16–21 polylactide arms can be attached to the surface of dendrimer initiator, and the molecular weight of polylactides can be controlled by variation of molar ratios of monomer to initiator and polymerization time. Thermal analysis indicates that the star-shaped polylactides possess lower glass transition temperature, melting point, crystallinity, and maximum decomposition temperature than those of linear polylactide. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Dendrimer initiator; Ring-opening polymerization; Star-shaped polylactide

1. Introduction

It is well known that the aliphatic polyester is one of the most widely utilized class of degradable polymers in the field of biomedical materials [1–6]. Among them, poly(L-lactide) (PLLA) has been extensively used for many medical purposes, such as suturing, drug delivery and bond fixture due to its good biocompatibility, high mechanical strength, and excellent shaping and molding properties [7–9]. However, PLLA suffers from the difficulty of controlled degradation based on its high crystallinity and induction of material defects based on lability of melt viscosity, so it is necessary to modify the physical properties of the polymer. The promising approaches to overcome these problems are the introduction of hydrophilic units to control the biodegradability and branched structure to stabilize the melt viscosity and/or decrease the crystallinity in PLLA [10]. Recently, Kim et al. reported the synthesis and degradation of end-group-functionalized polylactide and revealed that the thermal stability and degradation behavior of star-shaped polymers strongly depended on the type and number of terminal groups [11].

Meanwhile, the well-defined macromolecular architectures such as comb-like polymers [10,12–14], star-shaped polymers [15–19], star block polymers [20–22], hyperbranched and dendritic polymers [23–28] have been attracting much attention due to their various functions and properties resulting from their special three-dimensional structures. Among them, star-shaped polymers can always be synthesized by two different routes: the 'arm first' strategy [29] and the 'core first' approach [30,31] on the basis of a multifunctional core used as initiator. Nowadays the latter has been widely utilized to synthesize well-defined star polymers with a predetermined number of arms. Up to now, the syntheses of star-shaped polylactides and poly(lactide-*co*-glycolide)s with multifunctional initiators, such as glycerol [32,33], aminopropanediol or aminohydroxymethylpropanediol [34], pentaerythritol [11, 35–38], mannitol/sorbitol [39], star-shaped poly(ethylene glycol)s [21,40], polyglycerine [41] and stannous octoate catalyst have been investigated. However, dendrimer with functional hydroxyl groups for the synthesis of star-shaped PLLA has not been reported yet.

In this paper, the starburst PAMAM–OH dendrimer (generation 3, containing 32 surface hydroxyl groups) as functional macroinitiator for the synthesis of novel star-shaped polylactides in the presence of stannous octoate ($SnOct_2$) was investigated. Effects of molar ratios of

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monomer to initiator, monomer to catalyst, monomer conversion, and reaction temperature on the molecular weight of polymer were studied. In addition, the thermal properties of the synthesized star-shaped polymers were also investigated.

2. Experimental

2.1. Materials

L-lactide (Aldrich) was purified by recrystallization in dry toluene. Starburst PAMAM–OH dendrimer (generation 3) was obtained from Aldrich and used as received. Stannous octoate (Sigma) was distilled under reduced pressure before use. Toluene was distilled from metallic sodium and benzophenone. All the other reagents were of analytical grade and used without further purification.

2.2. Starburst PAMAM–OH dendrimer for the synthesis of star-shaped polylactides

The solution of third generation PAMAM–OH dendrimer (G3-OH) in methanol was accurately weighed and placed into a dried glass ampoule, then evaporated under vacuum at 50 °C for 8 h to remove the methanol completely. After L-lactide and stannous octoate were added, the ampoule was purged three times with dry nitrogen and sealed under vacuum. The bulk polymerization was carried out at 130 °C in an oil bath for 24 h with stirring. After reaction, the crude product was dissolved in chloroform, microfiltered through a 0.45 μm-pore membrane filter, and precipitated into cold methanol twice. The polymer G3-PLLA obtained was a white fine powder. The monomer conversion was determined gravimetrically.

IR (KBr): 3441 ($\nu_{\mathrm{N-H}}$ and $\nu_{\mathrm{O-H}}$), 2997 ($\nu_{\mathrm{C-H}}$), 2947 ($\nu_{\mathrm{C-H}}$), 1757 ($\nu_{\mathrm{C=O}}$(ester)), 1650 ($\nu_{\mathrm{C=O}}$(amide)), 1538 ($\delta_{\mathrm{N-H}}$(amide)), 1455 ($\nu_{\mathrm{C-H}}$), 1384 ($\nu_{\mathrm{C-nf>H}}$), 1271 ($\nu_{\mathrm{C(=O)-O}}$), 1092 ($\nu_{\mathrm{C-N}}$), 1047 ($\nu_{\mathrm{C-O-C}}$), 756 ($\delta_{\mathrm{N-H}}$), 672 ($\delta_{\mathrm{N-H}}$) cm^{-1}. ^{1}H NMR (DMSO-d_6, δ): 1.27 (m, terminal $\mathrm{CH(C}H_3\mathrm{)OH}$), 1.46 (m, $\mathrm{C}H_3$ of PLLA), 2.20 (m, $\mathrm{NCH_2C}H_2\mathrm{CO}$), 2.45 (m, $\mathrm{NHCH_2C}H_2\mathrm{N}$), 2.65 (m, $\mathrm{NC}H_2\mathrm{CH_2CO}$), 3.11 (m, $\mathrm{NHC}H_2\mathrm{CH_2N}$), 3.50 (t, $\mathrm{NHCH_2C}H_2\mathrm{OH}$), 4.04 (t, $\mathrm{NHCH_2C}H_2\mathrm{OCOCH(CH_3)}$), 4.20 (m, terminal $\mathrm{C}H\mathrm{(CH_3)}$-OH), 5.19 (m, $\mathrm{C}H$ of PLLA). ^{13}C NMR (DMSO-d_6, δ): 16.7 ($C\mathrm{H_3}$ of PLLA), 20.6 (terminal $\mathrm{CH(}C\mathrm{H_3)OH}$), 33.4 ($\mathrm{NCH_2}C\mathrm{H_2CO}$), 37.1 ($\mathrm{NH}C\mathrm{H_2CH_2N}$), 41.6 ($\mathrm{NH}C\mathrm{H_2CH_2OH}$), 49.8 ($\mathrm{N}C\mathrm{H_2CH_2CO}$), 52.4 ($\mathrm{NHCH_2}C\mathrm{H_2N}$), 60.1 ($\mathrm{NHCH_2}C\mathrm{H_2OH}$), 62.8 ($\mathrm{NHCH_2}C\mathrm{H_2OCOCH(CH_3)}$), 65.7 (terminal $C\mathrm{H(CH_3)OH}$), 68.9 ($C\mathrm{H}$ of PLLA), 169.0–170.2 ($C\mathrm{O}$ of PLLA), 171.5 ($C\mathrm{O}$ of dendrimer), 174.2 (terminal $C\mathrm{OCH(CH_3)OH}$).

2.3. Measurements

FTIR spectroscopic analyses were performed on a Perkin–Elmer 2000 spectrometer with KBr discs. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker dmx 300 MHz spectrometer in DMSO-d_6 at room temperature, using TMS as internal standard. The molecular weight and molecular weight distribution were measured on a Waters 150-C gel permeation chromatography equipped with three Waters Styragel columns (HT2 + HT3 + HT4) at 35 °C. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 ml/min, and polystyrene standards were used as calibrations. Differential scanning calorimetric analysis (DSC) was carried out on a Perkin–Elmer DSC7 series thermal analysis system with a heating rate of 20 °C/min under nitrogen atmosphere, relative to indium standards. Glass transition temperatures (T_g) were determined from the second run. The annealing of PLLAs was carried out at 80 °C after the specimen was melted at 160 °C for 5 min and followed by quenching in a DSC sample pan. Thermogravimetric analysis (TGA) was carried out on a Perkin–Elmer TGA7 thermogravimetric analyzer in the temperature range of 30–500 °C.

3. Results and discussion

3.1. Synthesis of star-shaped PLLAs with PAMAM–OH initiator and $SnOct_2$ catalyst

3.1.1. Effect of dendrimer initiator on polymerization

To investigate the effect of dendrimer initiator on polymerization, the ring-opening polymerization of L-lactide was carried out with G3–OH initiator and $SnOct_2$ catalyst in bulk at 130 °C. When various amounts of initiator were used, the results of polymerization are shown in Table 1. In Table 1, the molecular weight determined by ^{1}H NMR spectroscopy (M_n(NMR)) was calculated from the average chain length (DP) and average number of arms (n) of polylactides. The average chain length was determined by comparison of the average signal intensity ratios of methine protons of PLLA (5.19 ppm) to the terminal methine protons (4.20 ppm). The average number of arms was calculated from the average signal intensity ratios of reacted methylene protons of dendrimer (4.04 ppm) to the unreacted methylene protons (3.50 ppm), combined with the number of surface hydroxyl groups. The result reveals that 16–21 polylactide arms can be attached to the surface of PAMAM–OH dendrimer initiator. It is obvious that there are unreacted hydroxyl groups in the resulting star-shaped polymers, this may be attributed to the change in the density and distribution of hydroxyl groups on surface of dendrimer initiator and steric hindrance of attached polylactide chains [42].

Fig. 1 shows the relationship between the molecular weight and molar ratios of monomer to initiator. From Fig. 1, it can be seen that the number-average molecular weight of the resulting star-shaped polylactides linearly increases with the molar ratio of monomer to initiator, which indicates

Table 1
Effects of molar ratios of monomer to initiator to molecular weight and molecular weight distribution of PLLAs

Sample	$[LA]_0/[OH]_0$	Conversion (%)	M_n(GPC)[a]	M_w/M_n[a]	DP[b]	n[b]	M_n(NMR)[b]
1[c]		97.2	64,000	1.78	1000	1	72,000
2	200	95.0	83,400	1.64	148.2	18.5	204,000
3	150	93.6	58,700	1.52	105.6	20.8	165,000
4	100	92.4	46,250	1.75	76.1	20.0	116,500
5	50	85.6	32,960	1.80	49.5	18.0	71,000
6	25	77.5	19,540	1.85	31.6	17.6	47,000

Polymerization conditions: $[SnOct_2]/[LA] = 0.15{:}100$, 24 h at 130 °C.

[a] Determined by GPC analysis with polystyrene standards, THF was used as eluent.

[b] Determined by ^{1}H NMR analysis, $M_n(\text{NMR}) = 72 \times \text{DP} \times n + \text{MW(initiator)}$.

[c] Linear polylactide, prepared only using $SnOct_2$.

the role of the hydroxyl groups in dendrimer surfaces as effective propagation centers. Meanwhile, it is noted that the molecular weight determined by ^{1}H NMR is much higher than that obtained by GPC (M_n(GPC)), this is due to the unique molecular structure of star-shaped polymers. For star-shaped polymer, it is well known that the GPC analysis is not the method of choice to determine the molecular weight [26]. Since it has smaller hydrodynamic volume than that of linear polystyrene having the same molecular weight, the GPC analysis always underestimates the molecular weight of star-shaped polymers.

In this study, all polymers were synthesized under rigorously anhydrous conditions. The solution of dendrimer initiator in methanol was evaporated under vacuum at 50 °C for 8 h, to avoid an initiation by water and methanol, which will lead to a mixture of linear and graft polymers. In a typical run, the ratio of monomer to hydroxyl group is 150, and the polymerization initiated with PAMAM–OH (generation 3, containing 32 hydroxyl groups) was carried out at 130 °C in a sealed tube for 24 h. After purification, the polymer was obtained in 93.6% conversion. The GPC trace (Fig. 2) is symmetrical and monomodal, which suggests that no mixture of graft and linear polymers is formed [10]. Fig. 2 shows that the resulting star-shaped polymer has the M_n(GPC) value of 58,700 and polydispersity of 1.52. However, the molecular weight determined by NMR ($M_n(\text{NMR}) = 165{,}000$) is much larger than that obtained by GPC. Calculation of elemental analysis result: C 50.10%, H 5.71%, N 0.76% (calculated by M_n(NMR)); C 50.27%, H 5.92%, N 2.15% (calculated by M_n(GPC)). Found: C 50.12%, H 5.74%, N 0.88%. By comparing the above results, it can be seen that the measured value is closer to that calculated by M_n(NMR), which also indicates that the molecular weight determined by NMR is much closer to the real value.

The star-shaped polylactide obtained can be dissolved in general organic solvents such as chloroform, methylene chloride, benzene, toluene, THF, DMF, DMSO, however, it is poorly soluble in water, ether, alcohol and paraffin. Though the solution of star-shaped polylactides in chloroform is transparent, the signals of protons in poly(amideamine) (PAMAM) appear to be a broad peak and cannot be distinguished obviously in ^{1}H NMR spectra taken in $CDCl_3$. This phenomenon can be ascribed to the poor solubility of PAMAM in chloroform. In this study, the NMR spectra were taken in DMSO-d_6 because both PAMAM and polylactide can be well dissolved in this solution.

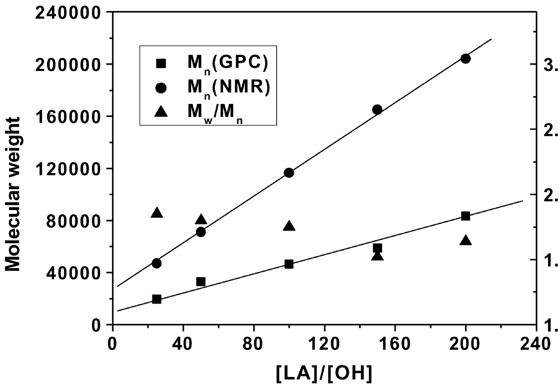

Fig. 1. Dependence of molecular weight on the molar ratio of monomer to hydroxyl group. Polymerization conditions: $[LA]/[SnOct_2] = 100{:}0.15$, 130°C, 24 h.

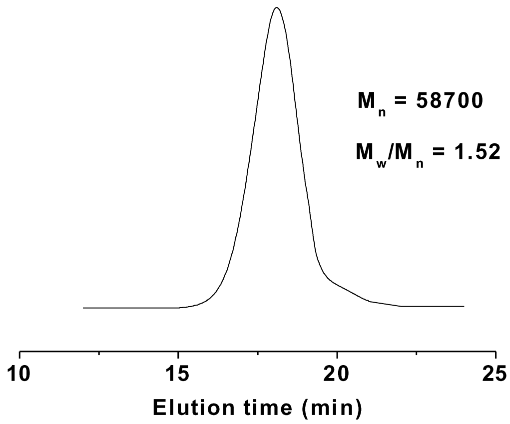

Fig. 2. GPC trace of star-shaped polylactide.

Table 2
Results of polymerization of L-lactide with different polymerization times in bulk at 130 °C and [OH]/[LA]/[SnOct$_2$] = 1:50:0.15

No.	Time (h)	Conversion (%)	M_n(GPC)	M_w/M_n	M_n(NMR)
1	0.5	18.8	9480	1.35	18,700
2	1	32.0	14,500	1.44	28,000
3	3	54.7	20,700	1.60	45,100
4	8	72.4	27,540	1.64	58,400
5	16	80.8	31,820	1.75	64,500
6	24	85.6	32,960	1.80	68,600

3.1.2. *Effect of monomer conversion on polymerization*

The results of polymerization of L-lactide using G3-OH initiator and SnOct$_2$ catalyst with different polymerization times are listed in Table 2. It is found that the molecular weight distribution increases with monomer conversion, which may be due to the change in the density and distribution of hydroxyl groups on globular polymer surface, transesterification and increasing viscosity with the increasing polymerization time. Fig. 3 shows that the molecular weight linearly increased with monomer conversion, which suggests that the molecular weight of star-shaped polylactides can be determined by controlling monomer conversion.

3.1.3. *Effect of SnOct$_2$ catalyst on polymerization*

Table 3 shows the influence of molar ratio of monomer to catalyst. From Table 3, it can be seen that the amount of SnOct$_2$ catalyst almost has no influence on the molecular weight of the resulting star-shaped polylactides. This also reveals that the hydroxyl-terminated dendrimer is the real initiator, which can stoichiometrically control the molecular weight of the star-shaped polymer. It is worth noting that with increasing molar ratio of monomer to catalyst, the polymerization rate becomes slow, while the molecular weight distribution slightly decreases. This can be attributed to the slow polymerization rate and the symmetry of the star-shaped polymer can be effectively controlled [35].

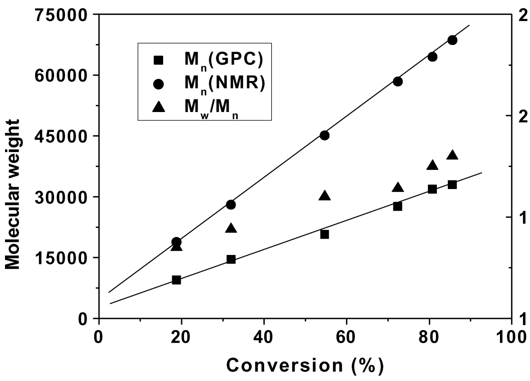

Fig. 3. Molecular weight and molecular weight distribution at various monomer conversions. Polymerization conditions are the same as Table 3.

Table 3
Results of polymerization of L-lactide with various amounts of SnOct$_2$ catalyst in bulk at 130 °C and [LA]/[OH] = 50

No.	[LA]/[SnOct$_2$]	Time (h)	Conversion (%)	M_n(GPC)	M_w/M_n	M_n(NMR)
1	100	12	84.8	28,760	1.84	66,500
2	200	12	83.6	30,150	1.72	65,300
3	400	12	81.4	30,630	1.69	62,500
4	600	12	80.4	30,100	1.65	62,800
5	1000	24	82.0	30,760	1.64	65,400
6	2000	24	81.5	31,840	1.60	63,200

3.1.4. *Effect of reaction temperature on polymerization*

To investigate the effect of reaction temperature on polymerization, the polymerization was carried out from 110 to 190 °C. Results of polymerization at different temperatures are presented in Table 4. It is found that the polymerization rate obviously increases with the increasing of reaction temperature. When the polymerization of L-lactide was conducted at different temperatures for 3 h, the molecular weight of the synthesized polylactides increased as the reaction temperature arose from 110 to 190 °C, and the corresponding molecular weight distribution became broad. When the polymerization was conducted at 190 °C, though the monomer conversion increased with increasing polymerization time, the molecular weight of polylactides decreased, and the corresponding molecular weight distribution ascended. The above results can be ascribed to transesterification and thermal degradation in the course of polymerization [10], which lead to increasing amounts of low molecular byproducts. As for polymerization of L-lactide using dendrimer initiator and SnOct$_2$ catalyst, 130 °C is found to be the most suitable reaction temperature. As previously described, the star-shaped polylactides obtained at this temperature had relatively narrow molecular weight distribution and almost controllable molecular weight, and the phenomenon of transesterification and thermal degradation during polymerization was not obvious. At lower temperatures, the solubility of dendrimer initiator in the melt of monomers was insufficient. At higher temperatures, the discoloration of the reaction products

Table 4
Effects of reaction temperature on molecular weight and molecular weight distribution

No.	Temperature (°C)	Time (h)	Conversion (%)	M_n(GPC)	M_w/M_n	M_n(NMR)
1	110	3	40.8	17,240	1.54	36,200
2	130	3	54.7	20,700	1.60	45,000
3	150	3	72.4	24,000	1.96	54,200
4	170	3	80.8	24,750	2.10	62,600
5	190	3	85.6	25,500	2.36	68,300
6	190	8	88.4	21,760	2.88	52,400
7	190	24	90.6	18,950	3.50	48,400

Polymerization conditions: [OH]/[LA]/[SnOct$_2$] = 1:50:0.15.

Table 5
Thermal properties of various polylactides determined by DSC and TGA

Sample	T_g (°C)	T_m (°C)	$\Delta H_m - \Delta H_c$ (J/g)	X_c (%)	T_{max} (°C)
1	59.6	176.6	38.5	41.1	307.3
2	57.6	127.5, 138.6	30.6	32.7	293.6
3	57.2	126.4, 136.0	29.2	31.2	290.5
4	56.9	126.0, 135.2	27.9	29.8	288.9
5	54.7	122.4, 129.5	23.1	24.7	287.2
6	50.8	111.5, 119.2	19.2	20.5	285.4

Samples are the same as Table 1.

could be observed, and the resultant polymers possessed broad molecular weight distribution and were only partially dissolved in chloroform.

3.2. Thermal properties of star-shaped polylactides

It is well known that star-shaped polymers have different physico-chemical properties compared with their linear counterparts owning to their unique molecular architecture. In this study, the thermal properties of star-shaped polylactides were investigated by DSC and TGA and compared with those of linear polylactide. In addition, influence of annealing at 80 °C on thermal properties of star-shaped polylactides was also studied.

3.2.1. DSC analysis of polylactides

The thermal properties of star-shaped polylactides and linear polylactide are listed in Table 5. The crystallinity (X_c) of polylactides was determined from DSC measurements by the equation $X_c = (\Delta H_m - \Delta H_c)/\Delta H_m^0$, with the aid of the enthalpy of fusion of 93.6 J/g for the perfectly crystalline PLLA [43]. From Table 5, it can be observed that the star-shaped polylactides possess lower glass transition temperatures (T_g), melting points (T_m) and crystallinity than those of linear polylactide. The low melting point of star-shaped polylactides obtained in the range of 100–140 °C can be attributed to the crystalline imperfections due to increased free end groups and branching points in the more branched polymers [21].

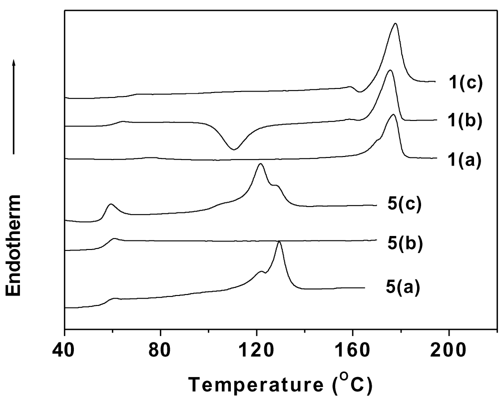

Fig. 4. DSC curves of (a) native, (b) melted, and (c) annealed polylactides (Samples 1 and 5).

Table 6
Dependence of thermal properties of polylactide (Sample 5) on annealing time

Time (h)	T_g (°C)	T_m (°C)	$\Delta H_m - \Delta H_c$ (J/g)	X_c (%)
1	53.6	119.6, 128.9	12.7	13.6
2	54.2	120.5, 129.0	22.0	23.5
3	54.4	120.8, 128.5	29.0	31.0
5	54.9	122.0, 128.7	34.4	36.8
8	55.1	122.5, 128.4	36.0	38.5
10	55.2	122.7, 128.1	36.2	38.7

As a comparison, the DSC curves of native, melted, and annealed samples are outlined in Fig. 4. These curves indicate the presence of a few characteristic transitions such as glass transition, cold crystallization and melting, which are typical for semi-crystalline polylactide samples. As for the star-shaped polylactides initiated with dendrimer initiator, however, the cold crystallization and melting peak of melt samples in the DSC curves cannot be observed. The result is attributed to the relatively slow crystallization rate. The existence of similar globular structure of star-shaped polylactides will decrease the intermolecular interaction and restrict the macromolecular conformation, which considerably refine the crystallization behavior of polymers. Meanwhile, it is noted that the star-shaped polymers have two melting signals, which can be observed often in semi-crystalline polymers [44–47]. The phenomenon is resulting from the crystallinities of different size and different degree of crystalline perfection.

3.2.2. Influence of annealing on thermal properties of star-shaped polylactides

To investigate the effect of annealing on thermal properties, the star-shaped polylactides were annealed at 80 °C for various times, and the results are shown in Table 6. With the increasing of annealing time, the glass transition temperatures and crystallinity increase gradually, and the distinction between two melting peaks is reduced. The result

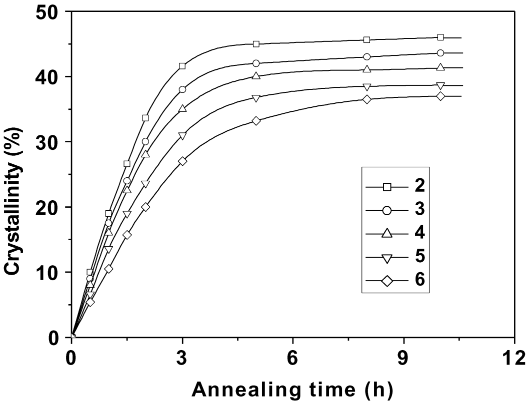

Fig. 5. Effects of annealing time on crystallinity of star-shaped polylactides. Numbers beside the curves indicate samples as shown in Table 1.

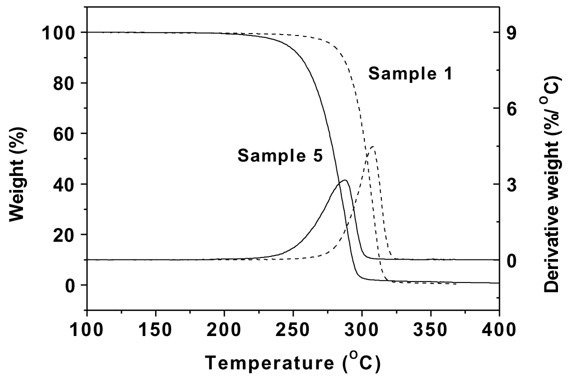

Fig. 6. TGA thermograms of star-shaped polylactide (Sample 5) and linear polylactide (Sample 1).

can be ascribed to the increasing crystallinities of different size and different degree of crystalline perfection.

It is reported that annealing of polylactide at temperatures above T_g is a promising way to achieve control over the crystallinity [47–49]. Fig. 5 shows the effects of annealing time on crystallinity of star-shaped polylactides. From Fig. 5, it can be seen that the crystallinity of polylactides increases with increasing of annealing times. When the annealing time is large than 8 h, the value of crystallinity is almost constant. It is worth noting that with increasing molecular weight, the crystallization rate increases, and the crystallinity of polymers can be controlled in a broader range. For instance, for Sample 2 (M_n(NMR) = 83,400) the proper adjustment of annealing time allows to obtain polymers with crystallinity in the range from 0 to 46.0%, whereas for Sample 5 (M_n(NMR) = 32,960) values of X_c can be regulated in the range from 0 to 38.7%.

3.2.3. TGA analysis of polylactides

The thermal stability of polylactides was determined by TGA. As shown in Table 5, the maximum decomposition temperature (T_{max}) of star-shaped polylactides is obviously lower than that of linear polylactide, and the value of T_{max} of star-shaped polylactides is reduced as the molecular weight decreases. As a comparison, the TGA thermograms of star-shaped polylactide (Sample 5) and linear polylactide (Sample 1) are outlined in Fig. 6. It can be observed that the star-shaped polylactide and linear PLLA start to decompose at about 210 and 250 °C, respectively. The maximum decomposition temperature and the corresponding derivative weight of Sample 5 are 287.2 °C and 3.15%/°C. As for Sample 1, the corresponding values of T_{max} and the maximum derivative weight are 307.3 °C and 4.88%/°C, respectively. The results indicate that the thermal stability of linear polylactide is excellent than that of star-shaped polylactides. The relatively poor thermal stability can be ascribed to the thermally unstable nature of hydroxyl-terminated polylactides, which are liable to decompose to form cyclic monomer [50].

4. Conclusions

The novel star-shaped polymers that consist of poly(L-lactide) (PLLA) arms and a starburst PAMAM–OH dendrimer core were successfully prepared by ring-opening polymerization of L-lactide in the presence of PAMAM–OH dendrimer (generation 3) and a catalytic amount of stannous octoate. Effects of molar ratios of monomer to initiator, monomer to catalyst, monomer conversion, and reaction temperature on polymerization were studied. The molecular weights of star-shaped polylactides can be controlled by change of molar ratios of monomer to initiator and polymerization time. Thermal analysis reveals that the star-shaped polylactides possess lower glass transition temperature, melting point, crystallinity, and maximum decomposition temperature than those of linear polylactide. When samples were annealed at 80 °C, the star-shaped plylactides with higher molecular weight exhibit faster crystallization rate and wider range of crystallinity.

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