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Synthesis, characterization and thermal properties of hexaarmed star-shaped poly(ε-caprolactone)-*b*-poly(D,L-lactide-*co*-glycolide) initiated with hydroxyl-terminated cyclotriphosphazene

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Abstract

Hexakis[*p*-(hydroxymethyl)phenoxy]cyclotriphosphazene was prepared by the reaction of hexachlorocycltriphosphaneze with the sodium salt of 4-hydroxybenzaldehyde and subsequent reduction of aldehyde groups to alcohol groups by using sodium borohydride. Hexaarmed star-shaped hydroxyl-terminated poly(ε-caprolactone) (PCL) were successfully synthesized via ring-opening polymerization of ε-caprolactone (CL) with the above hydroxyl-terminated cyclotriphosphazene initiator and stannous octoate catalyst in bulk. The number-average molecular weight of PCL linearly increased with the molar ratio of monomer to initiator. The star-shaped PCL with hydroxy end groups could be used as a macroinitiator for block copolymerization with D,L-lactide (D,L-LA) and glycolide (GA) using stannous octoate catalyst. IR, ^{1}H NMR and GPC analysis showed the star-block copolymers were successfully synthesized and the molecular weights and the unit composition of the star-shaped block copolymers were controlled by the molar ratios of D,L-LA and GA monomers to CL. The copolymer presented a two-phase structure, namely, PCL crystalline and D,L-LAGA amorphous domains, which made the copolymer different from linear PCL and star-shaped PCL in crystallinity and thermal behaviors.

Keywords: Phosphazene; Ring-opening synthesis; Star-shaped block copolymer

1. Introduction

Considerable interests exist in aliphatic polyesters owing to their excellent biodegradability and biocompatibility. Among them, homopolymers and copolymers of glycolide (GA), lactides (LA), and ε-caprolactone (CL) are especially interesting for their applications in the medical filed [1–5]. For example, poly(D,L-lactide-*co*-glycolide) (PLAGA) has been widely used as biodegradable sutures, implantable screws, intravascular stents, and drug delivery devices and as temporary scaffolds for tissue [6]. Poly(ε-caprolactone) (PCL) was also used as drug carrier because of its good drug permeability [7]. However, it was suitable for long-term drug delivery system owing to its high crystallinity and low degradation rate.

Polyesters with well-defined architectures such as star-shaped polymers [8–13], hyper-branched polymers [14,15], comb-like polymers [16–18] and dendrimers [19] are attracting increasing interests because of their unique structures and properties. Qiu et al. [20,21] successfully synthesized star block polyesters from pentaerythritol and trimethylolpropane as initiators. Hedrick et al. [22] reported the synthesis of dendrimer-like star polylactone using a hexahydroxy-functional compound initiator. Arvanitoyannis et al. [23] prepared novel polylactides with aminohydroxymethylpropanediol or aminpropanediol initiator. Pennings et al. [24] reported star-shaped polylactide-containing block copolymers with pentaerythritol initiator.

The effective synthesis method of polyesters is ring-opening polymerization. Stannous, zinc derivatives [25,26] and enzymes [27] have been successfully used as catalyst for the synthesis of aliphatic polyesters. However, stannous octoate [20,21] is the widely used catalyst for the production of biodegradable polyesters because it can produce high

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yield, molecular weight controlled, and narrow distributed polymers. Moreover, stannous octoate can avoid transesterification reaction and has lower biologic toxicity.

Phosphazenes are made up of a range of linear short chain or cyclic molecules and high polymers. They play an important role in the chemistry of heteroatom compounds [28]. Phosphazene polymers have attracted considerable attention because they can be tailored to possess a wide variety of physical and chemical properties by changing the side groups easily. Allcock et al. [29] reported the synthesis of polyphosphazene that can be used as carriers for drug delivery systems owing to their prominent biodegradability and biocompatibility. Cyclotriphosphazenes exhibit useful thermal and chemical properties such as flame retardancy, oil repellance and biocompatibility. Inoue et al. [30,31] reported the syntheses of star-shaped amino acids with cyclotriphosphazene core. It is reasonable to prepare star-shaped polymers possessing desired properties with cyclotriphosphazene cores because of unique structures and properties of them.

The star-shaped PCL-*b*-D,L-PLAGA copolymer could expectedly combined the excellent permeability of PCL and the higher biodegradability of the D,L-PLAGA block. Therefore, in this paper, a series of star-shaped PCL-*b*-D,L-PLAGA block polymers were synthesized by ring-opening polymerization with the hydroxyl-terminated cyclotriphosphazene compound as initiator. Then, thermal properties of these polymers were investigated.

2. Experimental

2.1. Materials

D,L-lactide and glycolide were gifts from Tong Ji University (Shanghai, China) and purified prior to use. ε-caprolactone (Purac Biochem, The Netherlands) was purified with CaH_2 by vacuum distillation in a nitrogen atmosphere. Hexachlorocyclotriphosphazene was purchased from Aldrich and recrystallized from dry hexane followed by sublimation twice prior to use. Sodium hydride (60% in mineral oil) was purchased from Rohm-Hass (USA) and used directly. Stannous octanoate (Nippon Polyurethane, Shanghai) was distilled under reduced pressure before use. 4-Hydroxybenzaldehyde and sodium borohydride were purchased from Shanghai Chemical Reagents Corp. (Shanghai, China) and used without further purification. Hexane and ethyl acetate were distilled from calcium hydroxide. Chloroform was dried with molecular sieves type 4A before use. Tetrahydrofuran was distilled from CaH_2 under dry N_2 purge.

2.2. Measurements

^1H and ^{31}P NMR spectra were obtained from a Varian Mercury Plus-400 NMR spectrometer (Varian, USA). The chemical shifts were relative to tetramethsilane at $\delta = 0$ ppm for protons. As for phosphorus chemical shifts, 85% H_3PO_4 was used as external standard. Infrared spectra (FT-IR) were recorded on a Perkin–Elmer 936 spectrometer (Perkin–Elmer, USA) with potassium bromide discs. The molecular weight and molecular weight distribution were measured on a Waters gel permeation chromatography equipped with three Waters Styragel columns (HR3+HR4+HR5) at 30 °C. Tetrahydrofuran (THF) was used as eluent and narrow-distributed polystyrene standards were used as calibrations. Differential scanning calorimetric analysis (DSC) was investigated on a Perkin–Elmer DSC7/DX thermal analysis system with a heating rate of 10 °C/min from −10 to120 °C under nitrogen atmosphere. Thermogravimetric analysis (TGA) was carried out on a TGA7/DX thermogravimetric analyzer with a heating rate of 10 °C/min from room temperature to 700 °C under nitrogen atmosphere.

2.3. Preparation

2.3.1. Synthesis of $N_3P_3(OC_6H_4\text{-}p\text{-}CHO)_6$

This compound was synthesized according to the literature with minor modification [32]. The reaction of hexachlorocyclotriphosphazene with the sodium salt of 4-hydroxybenzaldehyde (prepared from the reaction of sodium hydride with 4-hydroxybenzaldehyde) yielded $N_3P_3(OC_6H_4\text{-}p\text{-}CHO)_6$.The resulting product was purified by recrystallization from ethyl acetate. The yield of the resulting product was 88% and the melting point was 160 °C.

2.3.2. Synthesis of $N_3P_3(OC_6H_4\text{-}p\text{-}CH_2OH)_6$

This compound was obtained from the reaction of $N_3P_3(OC_6H_4\text{-}p\text{-}CHO)_6$ with sodium borohydride at room temperature. The resulting compound was obtained after evaporation of the solvents and recrystallization [33]. The yield of the resulting product was 79% and the melting point was 217–218 °C.

2.3.3. Synthesis of hydroxyl-terminated star-shaped poly(ε-caprolactone)s

Certain amounts of poly(ε-caprolactone), $N_3P_3(OC_6H_4\text{-}p\text{-}CH_2OH)_6$ and stannous octoate were added into a dried glass ampule. Then the ampule was purged three times with dry nitrogen and sealed under vacuum. Under stirring, the bulk polymerization was carried out at 115 °C for 24 h. The resulting product was dissolved in chloroform, microfiltered through a 0.45-μm-pore membrane filter and then precipitated in hexane for three times. The purified polymer was dried in a vacuum until constant weight.

2.3.4. Block copolymerization

Certain amounts of PCL with hydroxy end groups obtained above, glycolide, D,L-lactide and stannous octoate were sealed into a dried glass ampule under vacuum after deoxygeniating with dry nitrogen. The ampule was kept at 115 °C with stirring for 36 h. The crude product was dissolved in chloroform, microfiltered through a 0.45-µm-pore membrane filter and then precipitated in hexane for three times. The purified polymer was dried in a vacuum until constant weight.

3. Results and discussion

3.1. Synthesis of hydroxyl-terminated cyclotriphosphazene initiator

The synthesis of hydroxyl-terminated cyclotriphosphazene initiator was described in Scheme 1. The resulting compound was characterized by IR spectroscopy (Fig. 1), ^{31}P and ^{1}H NMR spectroscopy (Fig. 2) and elemental analysis.

3.2. Synthesis of hydroxyl-terminated star-shaped PCL

The ring-opening polymerization of CL was carried out with hexaarmed phosphazene initiator and stannous octoate catalyst in bulk at 115 °C. IR spectrum of the star-shaped PCL was shown in Fig. 3(d). The wide peak at 3450 cm^{-1} was the absorption of decreased hydroxyl groups because of polymerization. The intensive absorption peak at 1730 cm^{-1} was assigned to the carbonyl band of PCL. ^{1}H NMR spectrum of star-shaped PCL was shown in Fig. 4. Upon comparison to the spectrum of the star-shaped initiator, the peak assigned to the hydroxyl proton ($\delta = 5.24$ ppm, d in Fig. 2(b)) disappeared, whereas the peak assigned to methylene protons ($\delta = 4.45$ ppm) drifted downfield ($\delta = 5.04$ ppm) as a result of polymerization. The methylene proton signal ($\delta = 3.64$ ppm) showed that PCL was terminated by hydroxy end groups, according to the conclusion of Feijen [34]. Therefore, hexaarmed star-shaped PCL with hydroxyl end groups were successfully synthesized from the homopolymerization of CL with phosphazene initiator and stannous octoate.

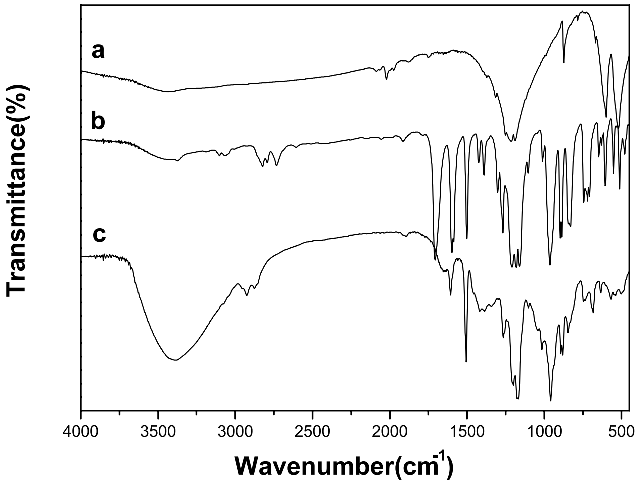
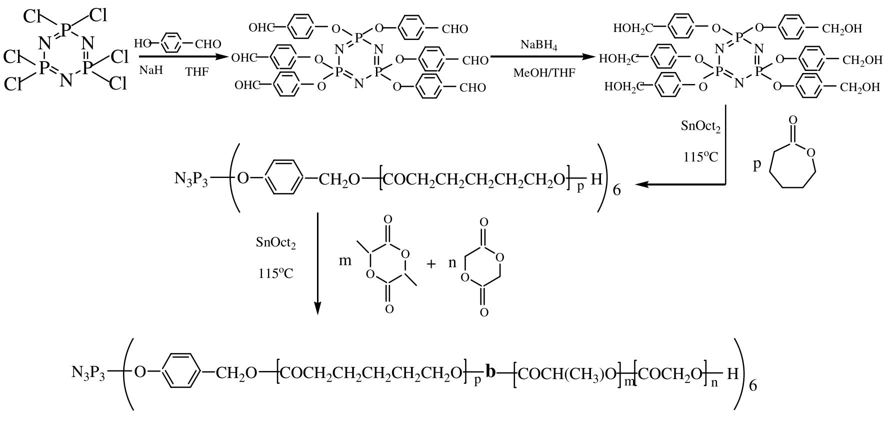


Fig. 1. IR spectrum of $N_3P_3Cl_6$ (a), $N_3P_3(OC_5H_5\text{-}p\text{-}CHO)_6$ (b) and $N_3P_3(OC_5H_5\text{-}p\text{-}CH_2OH)_6$ (c).

To obtain polymers with different molecular weight, various amounts of CL were used. The molecular weight determined by ^{1}H NMR spectroscopy was calculated from the integration ratio between the methylene protons in the repeat units (g) and the methylene protons in the terminal unit (h). As shown in Table 1, the number-average molecular weight of the resulting star-shaped PCL linearly increased with the molar ratio of monomer to initiator, which indicated that the hydroxyl-terminated phosphazene could be used as effective propagation centers. Moreover, the molecular weight determined by ^{1}H NMR was higher than that obtained by GPC but was close to the theoretic value, which could be ascribed to the unique molecular structure of star-shaped PCL. For star-shaped polymers, the GPC analysis is not the appropriate method to determine the molecular weight [35]. The GPC analysis always underestimates the molecular weight star-shaped polymers because it has smaller hydrodynamic volume than that of linear polystyrene having the same molecular weight.



Scheme 1. Synthesis of star-shaped polymers.

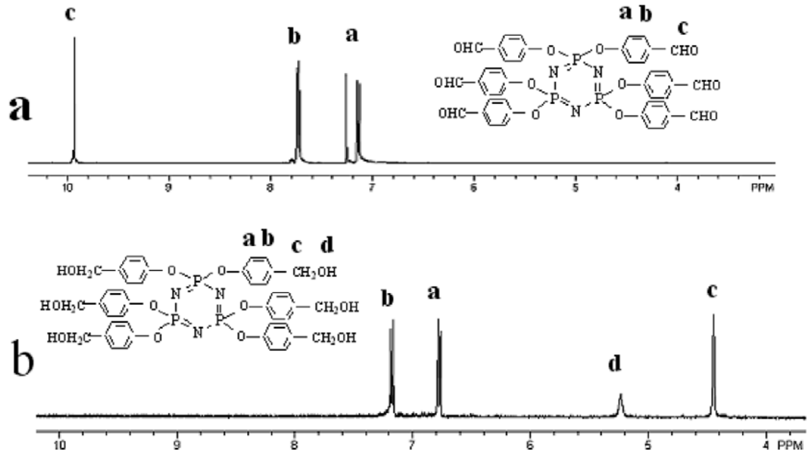


Fig. 2. ^{1}H NMR spectra of $N_3P_3(OC_5H_5\text{-}p\text{-}CHO)_6$ (a) and $N_3P_3(OC_5H_5\text{-}p\text{-}CH_2OH)_6$ (b).

Table 1

Results of the polymerization of $P_3N_3(OC_6H_5\text{-}p\text{-}OH)_6$ with various amounts of ε-caprolactone (CL) in bulk at and $[CL]/[SnOct_2]=1000$; polymerization time = 24 h

Sample	[CL]/[OH]	$M_{n,th}$[a]	M_{nNMR}[b]	M_{nGPC}[c]	M_w/M_n[c]	Conversion (%)
1	10	7600	7500	6400	1.051	98
2	20	14,400	14,100	11,000	1.083	99
3	30	20,800	19,500	16,400	1.165	97
4	40	27,100	24,900	21,100	1.252	96

[a] $M_{n,th}=[CL]/[OH]\times 6\times M_{CL}\times \text{Conversion}\%+M_{\text{initiator}}$, $M_{n,th}$ denotes the average number molecular weight of star-shaped poly(ε-caprolactone).

[b] M_{nNMR} was determined by ^{1}H NMR spectroscopy of star-shaped poly(ε-caprolactone).

[c] M_{nGPC} and M_w/M_n were determined by GPC analysis with polystyrene standards. THF was used as eluent.

3.3. Synthesis of star-shaped PCL-b-D,L-PLAGA

The hydroxyl-terminated PCL was used as a macroinitiator for the block copolymerization with D,L-LA and GA in bulk using stannous octoate as catalyst. IR spectrum of this polymer was shown in Fig. 3(e). The main difference of IR spectrum between the block copolymer and star-shaped PCL was in the carbonyl absorption band region. In the IR spectrum of the block copolymer, carbonyl absorption band became wide obviously and split into two peaks. The peak at 1762 cm^{-1} corresponded to the carbonyl absorption of PLA or PGA units, while the peak at 1730 cm^{-1} was assigned to the carbonyl absorption of PCL units. It was important evidence to prove that the PCL chains existed in the block copolymer as a block. ^{1}H NMR spectrum of star-shaped block copolymer was shown in Fig. 5. The peak assigned to methylene protons ($\delta=3.64$ ppm, h in Fig. 4) disappeared, and the new peaks at 4.35 and 4.15 ppm for the produced end groups of D,L-PLAGA block were observed. This indicated that the terminal hydroxyl groups of the macroinitiator successfully initiated the polymerization of D,L-LA and GA. The polymerization degree was estimated by comparison of the integration ratios of methine protons (h) and methylene protons (i) in the repeat units to those of methine protons (j) and methylene protons (k) in the terminal units. The calculated results (Table 2) demonstrated that molecular weights and the unit composition of the star-shaped block copolymers could be controlled by the molar ratios of D,L-LA and GA monomers to CL. The GPC traces of star-shaped PCL (samples 1 and 4) and star-shaped PCL-*b*-D,L-LAGA (sample 5) were shown in Fig. 6. These traces were symmetrical and monomodal, suggesting that no mixture of star and linear polymers was formed.

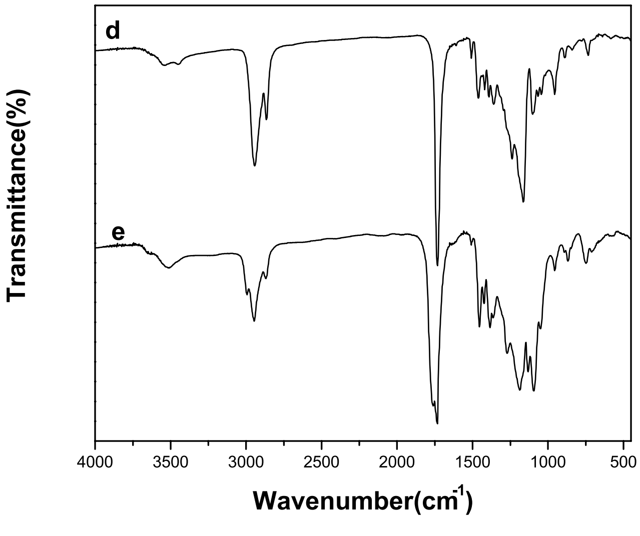


Fig. 3. IR spectra of star-shaped poly(ε-caprolactone) (PCL) with cyclotriphosphazene core (d) and star-shaped block copolymer: PCL-*b*-D,L-PLAGA (e).

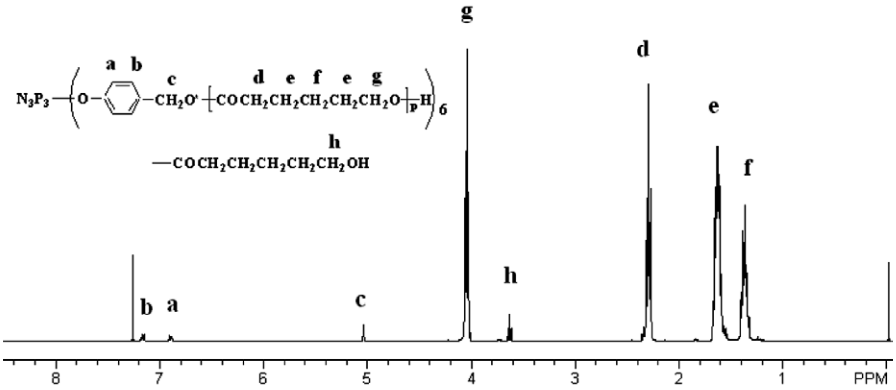


Fig. 4. ^{1}H NMR spectrum of star-shaped poly(ε-caprolactone) (PCL) with cyclotriphosphazene core.

Table 2
Results of block copolymerization at 115 °C and [CL]/[SnOct$_2$] = 1000; polymerization time = 36 h

Sample	[CL]/[LA]/[GA]	$M_{n,th}$	M_{nNMR}	M_{nGPC}	M_w/M_n	Conversion (%)
5	20/40/20	57,600	51,600	40,800	1.336	89
6	20/40/10	52,600	47,200	39,800	1.327	92
7	20/30/10	44,000	39,700	33,100	1.291	90
8	20/20/10	36,700	32,500	28,300	1.283	92

3.4. Thermal properties of star-shaped block copolymers

The thermal properties of star-shaped poly(ε-caprolactone)s and star-shaped block copolymers are presented in Table 3. According to the DSC data, melting point (T_m) and crystallinity (X_C) of linear PCL was higher than those of star-shaped PCL, which could be attributed to the crystalline imperfection mainly due to the short chain length of the star-shaped PCL arms. Moreover, the branched structure of star-shaped PCL should make contribution to the crystalline imperfection. In the branched star-shaped PCL, the chains of PCL were attached to a cyclotriphosphazene core; therefore, chain movements were hindered and their crystallizability was weakened, whereas no such steric hindrance existed in linear PCL. Star-shaped PCL-*b*-D,L-LAGA copolymer indicated the same tendency as the star-shaped PCL, such as the decrease of T_m and X_C. However, it could show unique thermal properties owing to the block structure in arms. The T_m and X_C of star-shaped PCL (sample 2) were 52.8 °C and 36.3% respectively, whereas the T_m and X_C of PCL block segments existed in star-shaped PCL-*b*-D,L-LAGA copolymer (sample 6) decreased to 38.7 °C and 3.1% respectively. These could be attributed to the presence of D,L-PLAGA block in the star-shaped block copolymer. It was well known that D,L-PLAGA was an amorphous copolymer because the copolymer was synthesized randomly from D,L-LA and GA. Therefore, the crystallinity of PCL segments was seriously hindered by amorphous D,L-PLAGA segments in the star-shaped copolymer. The branched structure of this block copolymer and the presence of D,L-PLAGA segments together led to the crystallinity imperfection which resulted in the obvious decrease of T_m and X_C of the block copolymer. With the increase of the D,L-PLAGA block length in copolymer, the

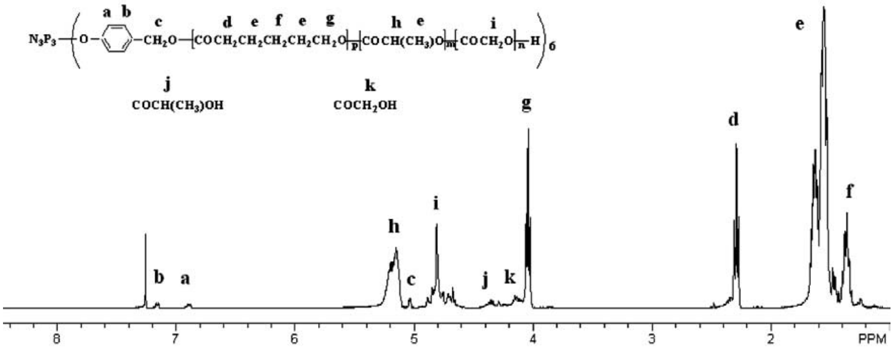


Fig. 5. ^{1}H NMR spectrum of star-shaped block copolymer: PCL-*b*-D,L-PLA GA.

Table 3
Thermal properties of star-shaped PCL and star-shaped PCL-*b*-D,L-PLAGA

Sample	$T_{m,onset}$ (°C)[a]	ΔH (J/g)[b]	X_c (%)[c]	T_{onset} (°C)[d]	T_{max} (°C)[e]
Linear PCL	61.0	76.3	54.7	376.9	396.5
1	45.2	41.2	29.5	320.7	378.6
2	52.8	50.6	36.3	357.7	398.8
3	54.6	54.8	39.3	378.2	408.9
4	57.5	56.9	40.8	385.4	413.5
5	40.5	3.0	2.2	298.3	342.6
6	38.7	4.3	3.1	269.7	320.2
7	39.3	6.8	4.9	268.4	316.2
8	41.2	9.4	6.7	259.4	307.8

Samples are the same as Tables 1 and 2.

[a] $T_{m,onset}$ denotes the onset melting point of PCL (samples 1–4) and PCL block segments (samples 5–8).

[b] Heat of melting of crystalline PCL (samples 1–4) and PCL block segments (samples 5–8).

[c] The degree of crystallinity of PCL (samples 1–4) and PCL block segments (samples 5–8). Calculated from the heat of melting using the melting of 139.5 J/g of 100% crystalline PCL.

[d] T_{onset} is the onset decomposition temperature.

[e] T_{max} is the temperature corresponding to the maximum rate of weight loss.

decrease of the degree of crystallinity occurred. Comparing to the star-shaped PCL, the star-shaped copolymer possessed a glass transition temperature (T_g), which could be ascribed to the presence of segments of D,L-PLAGA. In general, the glass transition temperature (T_g) moved to higher temperature with the increase of D,L-LA content. However, glass transition temperature (T_g) of some samples could not be determined because the T_g might be overlapped by the melting endotherm of PCL chains. All the information obtained from the DSC data could further prove that the PCL-*b*-D,L-LAGA copolymer contained two kinds of blocks, namely, PCL block and D,L-PLAGA block. Furthermore, the TGA data were also demonstrated that the T_{onset} of star-shaped poly(ε-caprolactone)s with short chain length (samples 1–2) was lower than that of the linear one, which could be attributed to the branched structure and short chain length of star-shaped PCL. But the T_{max} and T_{onset} of star-shaped poly(ε-caprolactone)s with long chain length (samples 3–4) were higher than those of poly(ε-caprolactone)s with short chain length. All of these should be ascribed to thermally stable cyclotriphosphazene core and the decrease of thermally unstable hydroxyl groups of star-shaped PCL. To the PCL-*b*-D,L-LAGA copolymer, the T_{onset} and T_{max} were lower than those of the star-shaped PCL owing to the comparative thermal instability of D,L-PLAGA segments in the star-shaped copolymer. Moreover, the thermal stability becomes poor with the reduction of molecular weight, which should be attributed to the increase of thermally unstable hydroxyl groups in copolymers. As shown in Fig. 7, the behavior of thermal decomposition of the star-shaped PCL-*b*-D,L-LAGA copolymer was different from that of the star-shaped PCL. The onset decomposition temperature of sample 2 was 357.7 °C and it presented a process of one-stage decomposition. However, the star-shaped PCL-*b*-D,L-LAGA copolymer showed a two-stage decomposition curve. The first stage should be ascribed to the decomposition of D,L-LAGA segments (T_{onset} = 268.4 °C, sample 7) while the second one should be attributed to the decomposition of PCL segments, which

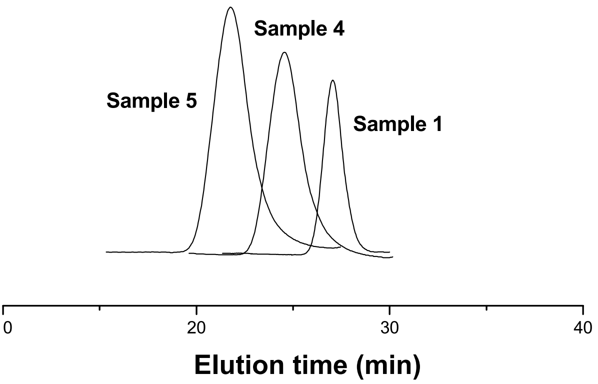


Fig. 6. GPC traces of star-shaped PCL (samples 1 and 4) and star-shaped PCL-*b*-D,L-LAGA (sample 5).

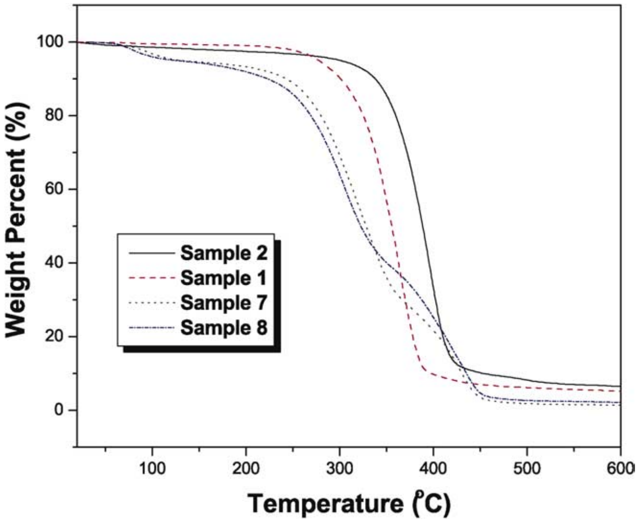


Fig. 7. TGA thermograms of star-shaped PCL (samples 2 and 1) and star-shaped PCL-*b*-D,L-PLAGA (samples 7 and 8).

could further confirm that two blocks (PCL and D,L-LAGA) were contained in the copolymer.

4. Conclusion

The novel star-shaped block copolymer PCL-*b*-D,L-LAGA with cyclotriphosphazene core was successfully synthesized by the block copolymerization of star-shaped PCL with hydroxyl end groups, D,L-LA and GA monomers using stannous octoate catalyst. The molecular weights and the unit composition of the star-shaped block copolymers were controlled by the molar ratios of D,L-LA and GA monomers to CL. The copolymer presented a two-phase structure, namely, PCL crystalline and D,L-LAGA amorphous domains, which made the copolymer different from the star-shaped PCL in crystallinity and thermal behaviors. Star-shaped block copolymer PCL-*b*-D,L-LAGA with cyclotriphosphazene core could be applied as biomaterials for its excellent biocompatible components. Further investigations are under way to determine the hydrolysis stability of the block copolymer.

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