

Design, Synthesis, and Characterization of a Potential Flame Retardant Poly(lactic acid-co-pyrimidine-2,4,5,6-tetramine) via Direct Melt Polycondensation

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ABSTRACT: Directly starting from D,L-lactic acid (LA) and pyrimidine-2,4,5,6-tetramine (PTA), the copolymer P(LA-co-PTA) as a novel potential solid compatible polymeric flame retardant is synthesized via melt polycondensation. When the molar feed ratio LA/PTA is 60/1, the optimal synthetic conditions are discussed. After the prepolymerization at 140°C for 8 h, using 0.5 wt % stannous oxide as the catalyst, the melt copolymerization at 160°C for 4 h gives the copolymer with the biggest intrinsic viscosity 0.88 dL g⁻¹. The structures and properties of P(LA-co-PTA)s at different molar feed ratios are characterized by FT-IR, ¹H-NMR, ¹³C-NMR, GPC, XRD, DSC, and TGA. The decomposition temperatures of P(LA-co-PTA)s are higher than these of homopolymer poly(D,L-lactic acid) (PDLLA). All copolymers have higher char yield than PDLLA, and the more PTA in the feed content, the higher char yield. What's more, there are some residues at 700–800°C, indicating that P(LA-co-PTA)s have good charring ability. When the monomer PTA is introduced into polylactic acid by chemical bonding as purine (PU) unit formed during the condensation, both the PTA's relatively higher nitrogen content and the PU's similar structure with flame retardant benzimidazole are beneficial to improve the thermal stability and charring ability, especially the latter. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40275.

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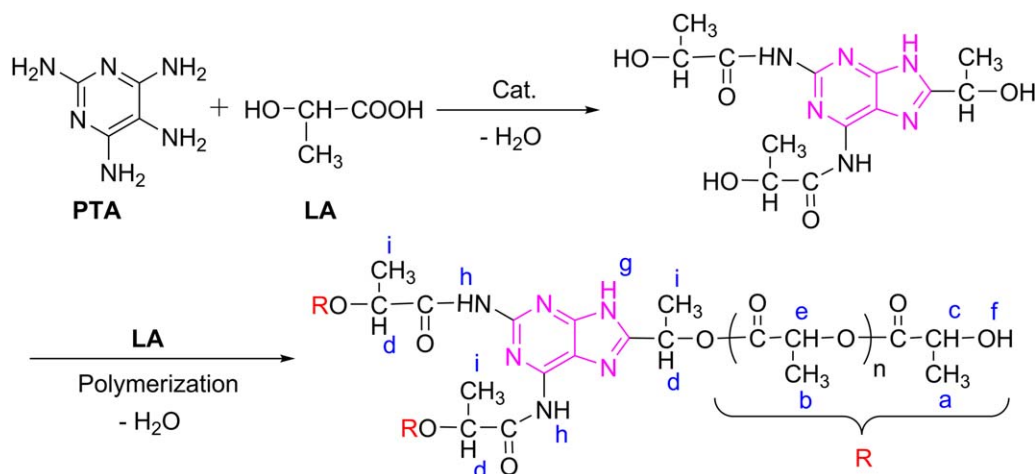
INTRODUCTION

Recently, more and more articles report the retardant modification of biodegradable material polylactic acid (PLA), and usually the modification method is the simple physical blending by using flame retardant as the additive. Due to the shortcomings of flame retardants, such as large adding dosage and poor compatibility, the original performance of the PLA materials is affected somewhat.^{1–6} If the flame retardant is introduced into PLA by chemical bonding, the inherent flame retardation of PLA can have very good flame-retardant effect. However, there are only a few researches on solid compatible polymeric phosphorus-containing PLA as flame retardant from a long synthetic route reported by Wang's group.^{7,8}

Due to the relatively short synthetic process without reaction solvent, the simple and efficient direct melt polycondensation of lactic acid (LA) is being received increasing attention in the synthesis of PLA materials.^{9–16} In our previous work, respectively using 3,3'-diaminobenzidine (DAB) and melamine (MA) as monomer for the direct melt copolycondensation with LA, we

have synthesized P(LA-co-DAB)¹⁷ and P(LA-co-MA).¹⁸ Due to the introduction of nitrogen series flame retardants, such as MA¹⁹ and benzimidazole²⁰ which is formed *in situ* by the reaction of LA with DAB during the direct melt polymerization,¹⁷ both P(LA-co-DAB) and P(LA-co-MA) significantly have better charring ability and thermal stability than the homopolymer poly(D,L-lactic acid) (PDLLA).^{17,18}

Comparing MA with DAB, MA obviously has higher nitrogen content than DAB, but for the resulted copolymer, P(LA-co-DAB) has better charring ability and thermal stability than P(LA-co-MA),^{17,18} which indicates that the benzimidazole unit should be important for the compatible polymeric flame retardant. If so, can the combination of this special structure with higher nitrogen content achieve a synergistic effect? To further explore the inherent flame retardation of PLA, herein we investigate the direct melt copolycondensation of LA with a new nitrogen series monomer pyrimidine-2,4,5,6-tetramine (PTA). Compared with MA, PTA has the same nitrogen atom number and the similar structure. Furthermore, during the melt copolymerization, a purine (PU) unit which is very similar with the



Scheme 1. The synthetic route of P(LA-co-PTA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

benzimidazole structure can be formed *in situ* in the copolymer P(LA-co-PTA) (Scheme 1). The experimental results show that this design and synthesis is successful.

EXPERIMENTAL

Materials

D,L-lactic acid (D,L-LA) was purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China), PTA was purchased from J&K Scientific (Beijing, China). All other chemicals, including *p*-toluenesulfonic acid (TSA), stannous chloride (SnCl₂), stannous oxide (SnO), zinc chloride (ZnCl₂), and zinc oxide (ZnO) were commercially available as analytical grades from Guangzhou Chemical Reagent Factory (Guangzhou, China). All these materials were used without further purification.

Instrumental Analysis and Measurements

Proton nuclear magnetic resonance (¹H-NMR) and Carbon-13 nuclear magnetic resonance (¹³C-NMR) spectra were recorded with a DRX-400 NMR spectrometer (Bruker instruments, Billerica, MA) with DMSO-*d*₆ as solvent and tetramethylsilane (TMS) as internal standard. Infrared spectra were obtained from a Fourier transform infrared (FT-IR) spectrometer (Bruker Vector 33, Ettlingen, Germany) by the dichloromethane liquid film method. The crystallinity of P(LA-co-PTA) was investigated by X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer (Bruker, Germany) using CuK_α radiation with a wavelength of 1.5418×10^{-10} m, and scanning range $2\theta = 5\text{--}50^\circ$ at a scanning speed of 0.03° at 5 s per step.

The intrinsic viscosity ($[\eta]$) of PLA modified by PTA was determined with Ubbelohde viscometer (Cannon-Ubbelohde, State College, PA) using chloroform (CHCl₃) as solvent at 25°C. According to the literature,^{10,21–24} the relative molecular weight and molecular weight distribution of the modified PLA were determined by gel permeation chromatography (GPC) (Waters 1515 pump, Torrance, CA) with tetrahydrofuran as solvent and with polystyrene (PS) as a reference at 40°C and a flow velocity 1 mL min^{-1} . Three Styragel HR columns from Japan covering a molecular weight range of $1 \times 10^3\text{--}10^6$ Da were used and calibrated using five PS narrow standards from BF Goodrich (Richfield, Ohio).

Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC7 thermal analyzer (Perkin-Elmer, Cetus Instruments, Norwalk, CT). The samples for DSC measurements (an average weight of 5 mg) were scanned at a heating rate of $10^\circ\text{C min}^{-1}$ under a nitrogen atmosphere (flow velocity 20 mL min^{-1}), then they were cooled to -50°C for 5 min and heated again to 200°C . The thermogravimetric analysis (TGA) was performed with STA-409PC thermal gravimetric analysis (Netzsch, Germany) at a heating rate of $10^\circ\text{C min}^{-1}$ under an air atmosphere (flow velocity 20 mL min^{-1}).

Melt Copolymerization

According to the previous work on melt copolymerization of LA,^{25–29} LA and PTA should be prepolymerized before copolymerization. After LA and PTA were uniformly mixed as pre-planned molar feed ratio, the obtained mixture was directly dehydrated for 8 h at 140°C under 4000 Pa in a flask equipped with mechanical stirring and thermometer. Then, the selected catalyst was added in according to the weight percent (wt %) of dehydrated reactants. The melt copolymerization was carried out at a certain temperature ($130\text{--}170^\circ\text{C}$) and an absolute pressure of 70 Pa for 2–10 h. When the reaction was finished, the reaction mixture was dissolved in CHCl₃ and then precipitated in a mixed solvent of methanol and distilled water (CH₃OH/H₂O). The polymer product was obtained as a white powder after the precipitate was collected and dried *in vacuo*.

RESULTS AND DISCUSSION

Using D,L-LA and PTA as starting materials, the copolymer P(LA-co-PTA)s with different molar feed ratios (LA/PTA = 15/1, 30/1, 60/1, 120/1) are directly synthesized via melt polycondensation after the conditions for the copolymerization are optimized. The structure and properties of these P(LA-co-PTA)s are characterized by FT-IR, ¹H-NMR, ¹³C-NMR, GPC, DSC, XRD, TGA, and viscosity $[\eta]$ measurements.

Optimal Synthetic Conditions for P(LA-co-PTA)

The melt copolycondensation of LA as a kind of esterification is a reversible and slow reaction when there is no catalyst at

Table I. The Effects of Catalyst Kinds on the Reaction

Run ^a	Catalyst	Product appearance	$[\eta]$ (dL g ⁻¹)	Yield (%)
1	ZnO	Yellow block	0.28	29
2	SnCl ₂	Yellowish powder	0.43	17
3	SnO	Yellowish powder	0.56	18
4	TSA	Yellow block	0.21	21
5	ZnCl ₂	Yellow powder	0.40	32

^aAll runs are polymerized with a molar feed ratio LA/PTA of 60/1, a polycondensation time of 6 h, a polycondensation temperature of 160°C and a catalyst quantity of 0.3 wt %.

atmospheric pressure. Generally, it is necessary to add the catalyst into the reaction system to accelerate the esterification. Therefore, we investigate the effects of different catalysts on the reaction firstly. According to the literature on the LA melt polymerization,^{14,16,30,31} five available catalysts are used, and their influences on the reaction are shown in Table I. It can be seen that the reaction catalyzed by SnO gives higher $[\eta]$ than that using other catalysts. This may be related to that this Tin catalyst as a Lewis acid with good water resistance not only has better catalytic effect for the formation of the PU ring, but also is suitable for the polymerization. Furthermore, the appearance of corresponding product is better (Run 3). Thus, SnO is selected as the catalyst in the following experiments, hoping to get a copolymer with a higher molecular weight.

The influences of the catalyst SnO dosage are shown in Table II. It can be seen that the $[\eta]$ reaches a maximum value when the weight percent of catalyst SnO quantity is 0.5 wt % of the prepolymer (Run 3). When the catalyst dosage is less, it is too insufficient to make the copolymerization complete. Meanwhile, excessive quantity of the catalyst is also unfavorable to the reaction, because the short-chain molecules are apt to be formed through the degradation of the polymer, which is also catalyzed by the metal catalyst.^{29,32} At the same time, the appearance of corresponding product is also acceptable in Run 3. Therefore, the suitable quantity of the catalyst SnO is 0.5 wt %.

The effects of melt copolymerization time on the reaction are shown in Table III. Obviously, the impacts of melt copolymerization time are quite significant. When the reaction system is at a high temperature for a long time, the oxidation and thermal degradation of polymer become serious, so the $[\eta]$ drops.^{26,32} Even when the melt copolymerization time is long

enough, the copolymer can be carbonized. Thus, to smoothly carry out the polymerization reaction to yield a copolymer with the higher molecular weight and the better appearance, the suitable melt copolymerization time should be 4 h (Run 3).

The influences of different melt copolymerization temperatures on the reaction are shown in Table IV. It can be seen that the $[\eta]$ does not increase with the increase of the temperature. Just when the temperature is 140°C, the $[\eta]$ reaches the maximum (Run 2). This indicates that the appropriate high temperature is beneficial to remove the water from the reaction system and promote the copolymerization. However, once the temperature is too high, the thermal degradation, even the carbonization may occur due to the reaction system at a high temperature for a long time.^{26,28,32}

Thus, when the molar feed ratio LA/PTA is 60/1, the appropriate conditions for the synthesis of the copolymer P(LA-co-PTA) via the direct melt copolycondensation are as follows: catalyst SnO quantity 0.5 wt %, reaction temperature 140°C and reaction time 4 h. In this case, the maximum $[\eta]$ is 0.88 dL g⁻¹ and the corresponding M_w is 7100 Da. Serial P(LA-co-PTA)s at different molar feed ratios are synthesized under the above optimal synthetic conditions.

Structure Characterization of P(LA-co-PTA)s

Taking the copolymer synthesized with a molar feed ratio LA/PTA of 60/1 as a representative, the FTIR curve of P(LA-co-PTA) is shown as Figure 1. The absorption at 3491 cm⁻¹ is assigned to stretching vibration of O—H, while the characteristic peaks at 3343 and 3212 cm⁻¹ are related to N—H bond in amide structure and PU ring (Scheme 1). The bands at 2994 and 2943 cm⁻¹ are assigned to the saturated C—H stretching

Table II. The Effects of Catalyst Dosage on the Reaction

Run ^a	Catalyst dosage (wt %)	Product appearance	$[\eta]$ (dL g ⁻¹)	Yield (%)
1	0.1	White block	0.45	34
2	0.3	Yellowish powder	0.56	18
3	0.5	Yellowish powder	0.66	24
4	0.7	Yellowish powder	0.30	32
5	0.9	Yellow block	0.21	14

^aAll runs are polymerized with a molar feed ratio LA/PTA of 60/1, a polycondensation temperature of 160°C, a polycondensation time of 6 h, and using SnO as the catalyst.

Table III. The Effects of Melt Polymerization Time on the Reaction

Run ^a	Time (h)	Product appearance	$[\eta]$ (dL g ⁻¹)	Yield (%)
1	2	White block	0.40	36
2	4	White powder	0.68	34
3	6	Yellowish powder	0.66	24
4	8	Mostly carbonized		
5	10	Almost entirely carbonized		

^aAll runs are polymerized with a molar feed ratio LA/PTA of 60/1, a polycondensation temperature of 160°C, and using 0.5 wt % SnO as the catalyst.

vibrations in the PLA chain, whereas their bending vibrations are observed at 1454 and 1382 cm⁻¹. A characteristic peak at 1755 cm⁻¹ is related to C=O bond in PLA chain, and the peaks at 1271, 1188, and 1093 cm⁻¹ are from C—O—C stretching vibration. Especially, the bands at 1630 and 1454 cm⁻¹ are the characteristic absorption peaks of the aromatic heterocyclic skeleton, so the PTA moiety as PU ring is introduced into the copolymer as designed indeed.

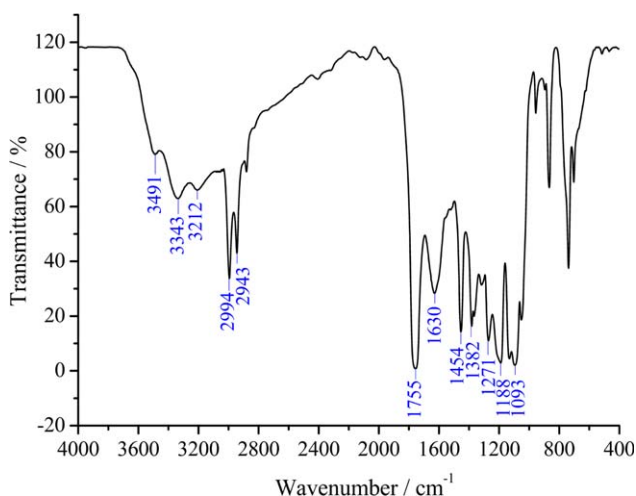
The data of ¹H-NMR spectrum of P(LA-co-PTA) synthesized as the molar feed ratio LA/PTA 60/1 (Figure 2) are obtained as follows. ¹H-NMR (DMSO-d₆ as solvent and TMS as internal reference), δ , ppm: 1.28 (H_a, CH₃ in terminal PLA segment), 1.47 (H_b, CH₃ in PLA chain), 1.63 (H_c, CH₃ in LA moiety close to PU ring), 4.21 (H_c, CH in terminal PLA segment), 4.96 (H_d, CH in LA moiety close to PU ring), 5.05–5.30 (H_e, CH in PLA chain), 5.52 (H_f, OH in terminal PLA segment), 8.32 (H_g, NH in amide bond), and 11.52–12.73 (H_g, NH in PU ring). Except for the peaks involving NH in amide bond and PU ring, all data are similar with the reported.⁷ Comparing the value of NH in amide bond with the literature (7.53–8.60),³³ it can be seen that the introduction of the PTA moiety into the copolymer is successful.

To further confirm the formation of the PU ring, the ¹³C-NMR spectrum of P(LA-co-PTA) synthesized as the molar feed ratio LA/PTA 60/1 is also recorded (Figure 3), and the data are obtained as follows. ¹³C-NMR (DMSO-d₆ as solvent and TMS as internal reference), δ , ppm: 16.89 (C_b), 19.88 (C_i), 20.77 (C_a), 65.91 (C_c), 68.97 (C_d, which is connected to PU ring), 69.11 (C_e), 69.34 (C_d, which is connected to NH in amide

Table IV. The Effects of Melt Polymerization Temperature on the Reaction

Run ^a	Temperature (°C)	Product appearance	$[\eta]$ (dL g ⁻¹)	Yield (%)
1	130	White block	0.70	46
2	140	White powder	0.88	47
3	150	White powder	0.73	37
4	160	White powder	0.68	34
5	170	Carbonized		

^aAll runs are polymerized with a molar feed ratio LA/PTA of 60/1, a polycondensation time of 4 h, and using 0.5 wt % SnO as the catalyst.

**Figure 1.** FTIR spectrum of P(LA-co-PTA) synthesized as the molar feed ratio LA/PTA 60/1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

bond), 124.07, 137.72, 144.78, 150.63, 155.37 (C in PU ring), 169.51 (C of C=O in terminal ester group), 169.65 (C of C=O in polyester chain), 172.22 (C of C=O close to PU ring). The data of C in C=O are similar with the reported.^{13,34} More importantly, the data of C in PU ring are also similar with the literature.³⁵

Therefore, the results of FTIR, ¹H- and ¹³C-NMR indicate that PTA moiety as the core is incorporated into the PLA backbone, and the obtained products are copolymers indeed. In fact, the formation mechanism of PU ring structure in the copolymer P(LA-co-PTA) is similar with that of the similar aromatic heterocyclic benzimidazole from the starting materials ortho aromatic diamine and LA,^{36,37} even under the condition of solvent-free and melting state.^{17,20,38,39} In a word, the copolymer P(LA-co-PTA) with a three-armed PLA structure using the PU structure as the core (Scheme 1) is formed as designed indeed. However, the following results show that the structure of the copolymer P(LA-co-PTA) is also related to the molar feed ratios somewhat.

The Effects of Molar Feed Ratios on the Molecular Weight

The GPC results of these P(LA-co-PTA)s with different molar feed ratios (LA/PTA) are shown in Table V. It can be seen that, compared with the homopolymer PDLLA, most copolymer samples have smaller molecular weight. This indicates that the introduction of PTA as a monomer containing the reactive amino is not beneficial to the direct melt copolymerization, and this conclusion is similar with the reported before.^{40–42} However, only sample C3 has bigger M_n and M_w than PDLLA synthesized under the same reaction conditions, this is related to the formation of multi-core structure in copolymer, which will be discussed in the following.

If the GPC results are compared with the corresponding M_T (Table V, the theoretical value of molecular weight calculated from the molar feed ratio), in most cases, the value of M_n is smaller than that of M_T . The reason is similar with the reported

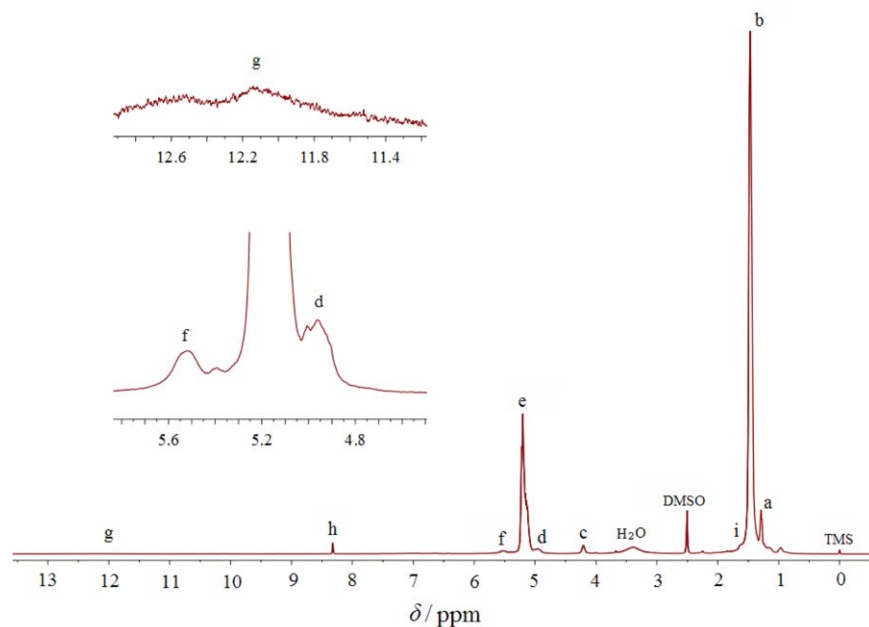


Figure 2. $^1\text{H-NMR}$ spectrum of P(LA-co-PTA) synthesized as the molar feed ratio LA/PTA 60/1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

before too, involving in the escape of LA out of the reaction systems as lactide during the direct melt copolycondensation,²⁷ and this is also the reason why the yields of PDLLA and P(LA-co-PTA)s are relatively lower. However, in some cases, the value of M_w is bigger than that of M_T . Even for sample C1, M_w can be twice of M_T . These also indicate that the multicore structure in copolymer is formed.

At the same time, it can be found that, with the increase of LA feed ratio, the change tendency of M_n , M_w , and polydispersity index (PDI, M_w/M_n) of all these copolymers is basically consistent with that of $[\eta]$. However, when the molar feed ratio LA/PTA is 60/1 (sample C3), though the $[\eta]$ is not the biggest, M_n , M_w , and PDI are reaching the maximum. Thus, the phenomenon of M_w peak value exists indeed. This may be related to the

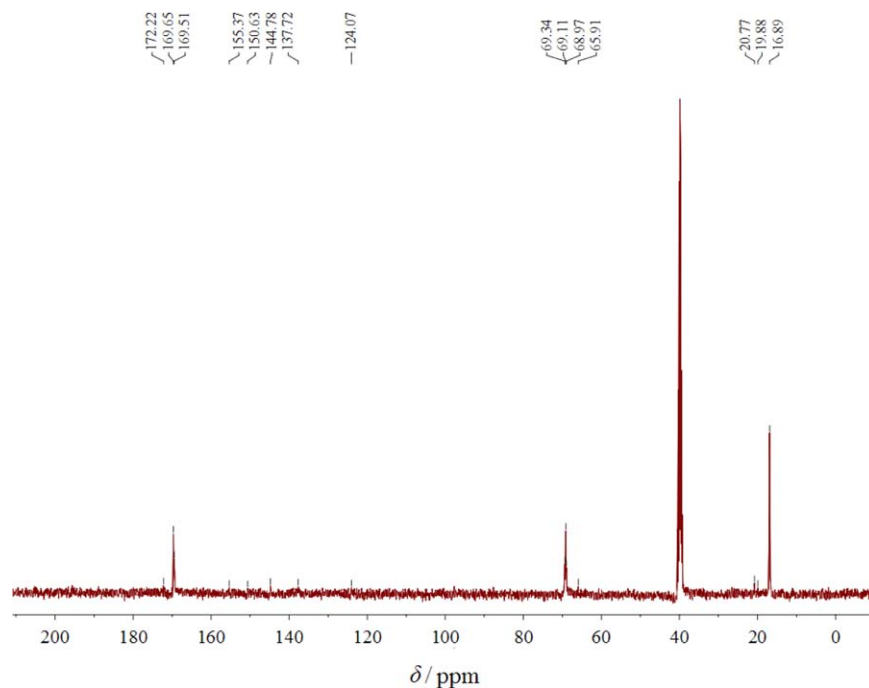


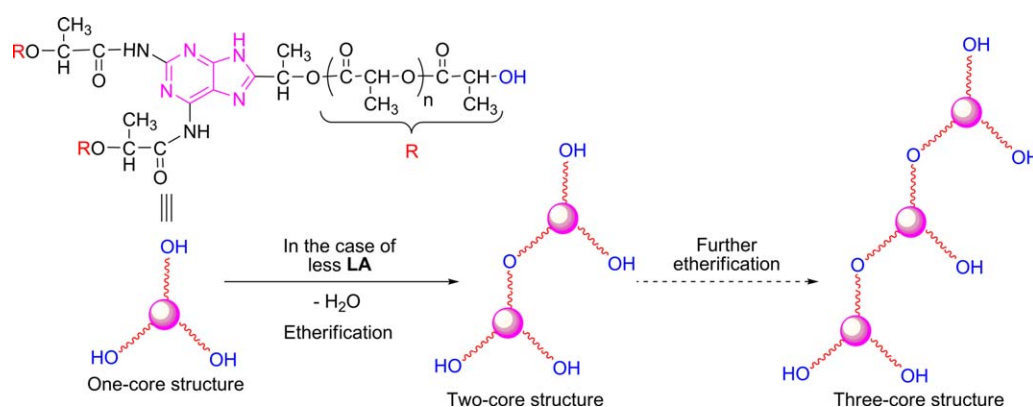
Figure 3. $^{13}\text{C-NMR}$ spectrum of P(LA-co-PTA) synthesized as the molar feed ratio LA/PTA 60/1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. The Effects of Different Molar Feed Ratios on Yield, $[\eta]$, and M_n of the Copolymers

Samples ^a	LA/PTA (molar feed ratio)	PTA content in feed (wt %)	Product appearance	$[\eta]$ (dL g ⁻¹)	Yield (%)	M_T (Da)	M_n (Da)	M_w (Da)	PDI ^b
C1	15/1	9.4	Yellow powder	0.32	33	1300	2000	2800	1.40
C2	30/1	4.9	Yellowish powder	0.55	41	2300	2100	3000	1.43
C3	60/1	2.5	White powder	0.88	47	4500	3400	7100	2.09
C4	120/1	1.3	White powder	0.90	49	8800	2600	4700	1.81
PDLLA	100/0	0	White powder	1.13	52	7300	3300	5500	1.67

^aAll samples are obtained under the optimized conditions, such as a polycondensation temperature of 140°C, a polycondensation time of 4 h, and using 0.5 wt % SnO as the catalyst.

^b M_T is the theoretical molecular weight as molar feed. The peak shape in all GPC curves is only a single peak.



Scheme 2. The formation of copolymer with multicore structure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

formation of multicore structure in copolymer via ether bond²⁶ during the direct copolymerization (Scheme 2).

According to the previous method for the calculation of molecular weight from the ¹H-NMR data and the way to investigate the copolymer with multi-core structure,^{25–27,43} the results here show that the sample C1 is mainly a two-core copolymer (Scheme 2), while samples C2–C4 simultaneously contain both two-core and one-core structures. For the existence of the M_w peak value in sample C3, the reason is similar with the previous research results that the M_w value of the copolymer with multicore structure is dependent on the core-number and the arm length.^{25–27,43}

From sample C2 to C4, the ratio of the two-core structure is gradually decreased. However, with the increase of LA feed ratio, the arm length is gradually increased. In sample C2, although the content of the two-core structure copolymer is relatively more, the arm length is too shorter to yield the biggest $[\eta]$ and M_w . In sample C4, although arm length is longer, the ratio of two-core structure is too less. Only in sample C3, the arm length is long enough and the ratio of two-core structure is also suitable, both are beneficial to the biggest M_w . Therefore, the PDI of sample C3 is the biggest of all, while it has a slightly lower $[\eta]$ than sample C4. In fact, this also indicates that

there are more two-core structure copolymers in sample C3 than C4.²⁶

The Effects of Molar Feed Ratios on the Crystallinity

The crystallinity of biodegradable polymers has great impact on their physical properties, especially their degradability. The XRD measurement results of the PLA copolymers modified by PTA

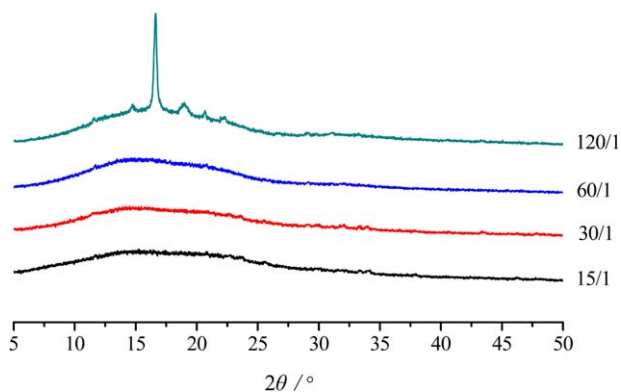


Figure 4. The XRD spectra of P(LA-*co*-PTA)s with different molar feed ratios (LA/PTA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table VI. The XRD and DSC Results of P(LA-co-PTA)s with Different Molar Feed Ratios (LA/PTA)

Sample (LA/PTA)	T_g (°C)	2θ (°)		X_c (%)	Crystallite dimension (10^{-10} m)	
		Face 110	Face 020		L_{110}	L_{020}
C1 (15/1)	45.5			Wholly amorphous		
C2 (30/1)	44.4			Amorphous		
C3 (60/1)	48.9			Amorphous		
C4 (120/1)	38.9	16.6	19.0	6.4	271.4	183.5
PDLLA ⁴⁴	54.6	16.7	19.0	20.8	154.4	83.9

with different molar feed ratios are shown in the Figure 4. It is obvious that only when the molar feed ratio LA/PTA is 120/1, the copolymer has the diffraction peaks at 16.6° and 19.0° . Compared with the homopolymer PDLLA synthesized via direct melt polycondensation,⁴⁴ the position of the XRD absorption peaks is basically similar (Table VI). This indicates that the main structure of sample C4 is one-core structure, and the relatively more regular structure than multicore structure may lead its similar crystallinity with the linear PLA somewhat. These results further prove the above conclusion that the structures of P(LA-co-PTA)s are changed with different molar feed ratios.

However, sample C4 as a kind of star-shaped PLA has a lower crystallinity (X_c , %) than the linear PLA (Table VI). Even so, the partial crystalline copolymer P(LA-co-PTA) synthesized as the molar feed ratio LA/PTA 120/1 has bigger crystallite dimension than PDLLA (Table VI). Therefore, the introduction of PTA into the PLA chain has an important influence on the crystalline property of PLA material, and it is possible to adjust the crystalline property and molecular weight of copolymers by changing the molar feed ratios.

Thermal Properties of P(LA-co-PTA)s

Thermal properties of P(LA-co-PTA)s are investigated by DSC and TGA. The DSC data are shown in Table VI. It can be seen that the glass transition temperature (T_g) of P(LA-co-PTA)s are

lower than that of the homopolymer PDLLA with a linear structure.⁴⁴ This may be related to the star structures of those P(LA-co-PTA)s, and the basic change tendency of T_g caused by the different structures is consistent with the literature.^{9,45–47} What's more, the T_g of the samples C1–C3 is basically close to 46°C and higher than that of sample C4, also indicating that the main structure in samples C1–C3 as two-core copolymer is different from the main one-core structure in sample C4. Relatively, the regularity of the multi-core copolymers is poorer, and every whole molecule has a greater rigidity, which is not beneficial to the motion of the molecular segment. Therefore, when $\text{LA/PTA} \leq 60 : 1$, the T_g of the copolymers is higher.

The more important thermal properties of P(LA-co-PTA) as a potential solid compatible polymeric flame retardant are investigated by thermogravimetry (TG). Taking the copolymer P(LA-co-PTA) synthesized with a molar feed ratio LA/PTA of 60/1 as a representative, its TG-DTG curve (Figure 5) shows that the differential thermogravimetry (DTG) curve has two peaks, this suggested that copolymers have two-step thermal degradation, while the PDLLA only has one peak in the DTG curve.¹⁷ This suggests that the decomposition of P(LA-co-PTA) is different from the PDLLA's decomposition, which is only a one-step thermal degradation.¹⁷ As a two-step thermal degradation, the first step in the decomposition of P(LA-co-PTA) is the thermal

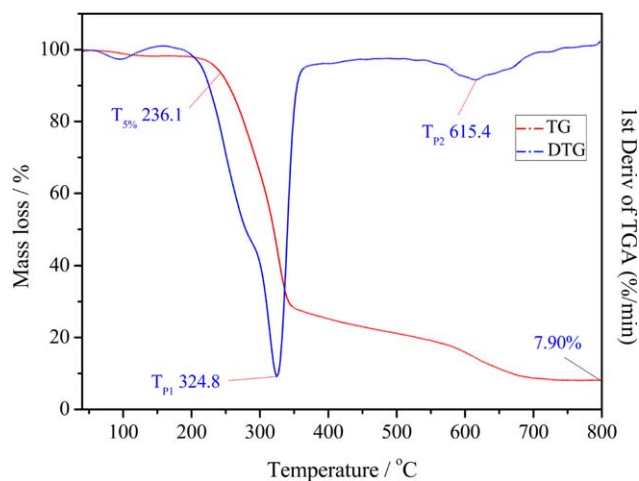


Figure 5. TG-DTG curve of P(LA-co-PTA) synthesized as the molar feed ratio LA/PTA 60/1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

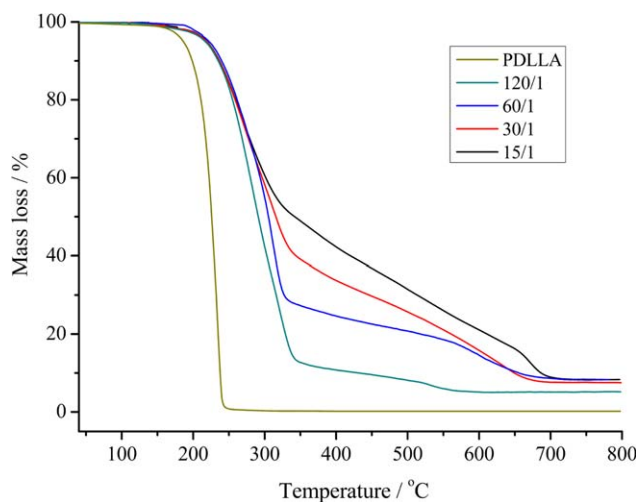


Figure 6. TG curves of P(LA-co-PTA)s with different molar feed ratios (LA/PTA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table VII. The Thermal Decomposition Temperatures of P(LA-co-PTA)s with Different Feed Molar Ratios (LA/PTA)

Samples (LA/PTA)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_{p1} (°C)	T_{f1} (°C)	T_{p2} (°C)	T_{f2} (°C)
C1 (15/1)	183.7	206.3	303.0	316.4	674.2	687.2
C2 (30/1)	178.3	203.6	310.8	337.6	642.2	669.5
C3 (60/1)	209.8	233.4	295.1	340.7	615.4	659.8
C4 (120/1)	207.2	225.1	291.4	336.5	538.2	555.2
PDLLA ^a	186.8	199.0	234.8	254.9	-	-
IFR-PLA1 ^b	235	-	271	-	-	-
IFR-PLA4 ^b	250	-	279	-	-	-

^aPDLLA used as comparative sample is polymerized under the same conditions, such as a polycondensation temperature of 140°C, a polycondensation time of 4 h, and using 0.5 wt % SnO as the catalyst.

decomposition of PLA chain, the second step is the decomposition of residual copolymer containing PU moiety. Compared with the instantaneous splitting of the entire polymeric chain in PDLLA's thermal decomposition,¹⁷ this difference shows that the copolymer P(LA-co-PTA) is more difficult to decompose under common heating conditions, and proves that P(LA-co-PTA) may be a potential polymeric flame retardant applied for PLA materials as well.

More importantly, the TG curve of the copolymer P(LA-co-PTA) synthesized as molar feed ratio LA/PTA 60/1 shows that, even at 800°C, there is still a char yield of 7.90% (Figure 5). This also indicates that P(LA-co-PTA) can be a potential polymeric flame retardant. Furthermore, when the molar feed ratio is different, these curves of P(LA-co-PTA)s are similar (Figure 6). The above conclusion is further confirmed by the data from these curves (Tables VII and VIII).

From Table VII, it can be seen that, compared with the corresponding data of the comparative sample PDLLA polymerized under the same conditions, all $T_{5\%}$ (the decomposition temperatures of 5% weight loss), $T_{10\%}$ (the decomposition temperatures of 10% weight loss), T_{p1} (the corresponding temperature of the first peak in the DTG curve), and T_{f1} (the final temperature of the first thermal decomposition stage) of the copolymers are higher. These results imply that the thermal stability of the PLA materials is improved when introducing the PU structure into the PLA chain.

From the point of charring ability (Table VIII), obviously, there is no residue of PDLLA for the complete thermal degradation when the temperature just reaches 375°C. And usually, for the same P(LA-co-PTA) samples (such as copolymer C4), with the increase of the temperature after 375°C, the char yield is decreased. However, P(LA-co-PTA) can give some residues even when the temperature reaches 700 or 800°C, and all char yields are still bigger than 5%. These suggest that the charring ability of P(LA-co-PTA) is obviously better than PDLLA due to the existence of PU unit in the copolymer. What's more, the more PTA in the feed ratio, the more PU unit introduced into the copolymer, the bigger char yield basically (Table VIII).

Similarly, the more PU unit contained in the copolymer, the higher T_{p2} (the corresponding temperature of the second peak in the DTG curve) and T_{f2} (the final temperature of the second thermal decomposition stage) (Table VII). These imply that the charring ability and the second stage degradation temperature are mainly controlled by the content of PU unit in the copolymer. However, the thermal stability of the copolymer depends on the M_w of P(LA-co-PTA) and the content of PU unit in the copolymer. So, with the increase of LA content in the molar feed ratio, the first stage degradation temperatures are not simply increased or decreased, but the sample C3 has the highest $T_{5\%}$, $T_{10\%}$, T_{p1} , and T_{f1} (Table VII).

Of course, compared with the inherent flame retardation of the phosphorus-containing PLA synthesized by Wang's group,⁸ the

Table VIII. The Char Yields of P(LA-co-PTA)s with Different Feed Molar Ratios (LA/PTA) at Different Thermal Decomposition Temperatures

Samples (LA/PTA)	Char yield (%)						
	375°C	400°C	450°C	500°C	600°C	700°C	800°C
C1 (15/1)	45.08	41.87	36.47	31.07	21.70	9.59	7.96
C2 (30/1)	36.03	33.61	29.57	25.53	15.64	7.52	7.38
C3 (60/1)	26.38	25.08	22.85	20.93	15.72	8.59	7.90
C4 (120/1)	11.43	10.68	9.46	8.03	5.19	5.10	5.03
PDLLA ^a	0	0	0	0	0	0	0
IFR-PLA1 ^b	6.8	4.8	2.2	-	-	-	-
IFR-PLA4 ^b	15.6	11.0	3.1	-	-	-	-

^aPDLLA used as comparative sample is polymerized under the same conditions, such as a polycondensation temperature of 140°C, a polycondensation time of 4 h, and using 0.5 wt % SnO as the catalyst.

thermal stability is basically similar (Table VII), but P(LA-co-PTA)s obviously have the higher char yields (Table VIII). What's more, our data are obtained under an air atmosphere, while the literature data are tested under a nitrogen atmosphere.⁸ Usually, the thermal stability of polymer in air is somehow lower than that in nitrogen. And noticeably, the situation that polymer has been exposed in air is more common than in nitrogen during real processing and application.^{48,49} Therefore, these also indirectly indicate that P(LA-co-PTA) has a good charring ability. If it is blended with PLA, it may have better flame retardant effect for PLA material.

At the same time, compared with P(LA-co-MA) synthesized from the cyclic monomer with the same nitrogen atom number and the similar structure, the thermal stability of P(LA-co-PTA)s is basically higher, and the charring ability is obviously improved. Even at the same thermal decomposition temperatures, the char yield of P(LA-co-PTA)s is several times bigger than that of P(LA-co-MA).¹⁸ However, compared with P(LA-co-DAB) containing the similar fused heterocycle, the thermal stability of P(LA-co-PTA) is slightly lower, but P(LA-co-PTA) has the higher charring ability, even its char yield at 800°C is three times of the P(LA-co-DAB)'s char yield at the 600°C.¹⁷ Thus, the anticipated results are achieved.

It is worth noting that, the use of PU structure in improving the thermal stability of polymers is mentioned only in a few reports in the past decades.⁵⁰ Therefore, these investigations will provide not only a novel route for the PLA material flame retardation, but also more possible application of PU ring compounds in flame retardants.

CONCLUSIONS

Directly starting from LA and PTA, P(LA-co-PTA) as a potential compatible solid polymeric flame retardant containing PU moiety is synthesized via melt polycondensation as designed for the first time. The structures and properties of P(LA-co-PTA)s at different molar feed ratios are characterized by FT-IR, ¹H-NMR, ¹³C-NMR, GPC, XRD, DSC, and TGA. The molecular weight, thermal stability, and charring ability can be controlled by synthetic conditions and different molar feed ratios. The introduction of PTA containing the higher nitrogen content into PLA by the method of chemical bonding and the formation *in situ* of PU structure with the similar structure to benzimidazole ring make the modified PLA copolymer have better thermal stability and higher char yield, especially the latter.

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REFERENCES

1. Bourbigot, S.; Fontaine, G. *Polym. Chem.* **2010**, *1*, 1413.
2. Fukushima, K.; Murariu, M.; Camino, G.; Dubois, P. *Polym. Degrad. Stab.* **2010**, *95*, 1063.
3. Li, S. M.; Ren, J.; Yuan, H.; Yu, T.; Yuan, W. Z. *Polym. Int.* **2010**, *59*, 242.
4. Tang, G.; Wang, X.; Xing, W. Y.; Zhang, P.; Wang, B. B.; Hong, N. N.; Yang, H.; Song, L. *Ind. Eng. Chem. Res.* **2012**, *51*, 12009.
5. Dasari, A.; Yu, Z. Z.; Cai, G. P.; Mai, Y. W. *Prog. Polym. Sci.* **2013**, *38*, 1357.
6. Kiuchi, Y.; Iji, M.; Yanagisawa, T.; Shukichi, T. *Polym. Degrad. Stab.*, to appear. DOI: 10.1016/j.polymdegradstab.2013.05.013.
7. Wang, D. Y.; Song, Y. P.; Lin, L.; Wang, X. L.; Wang, Y. Z. *Polymer* **2011**, *52*, 233.
8. Yuan, X. Y.; Wang, D. Y.; Chen, L.; Wang, X. L.; Wang, Y. Z. *Polym. Degrad. Stab.* **2011**, *96*, 1669.
9. Abiko, A.; Yano, S.; Iguchi, M. *Polymer* **2012**, *53*, 3842.
10. Jiang, W.; Huang, W.; Cheng, N.; Qi, Y. B.; Zong, X. P.; Li, H.; Zhang, Q. X. *Polymer* **2012**, *53*, 5476.
11. Mehtio, T.; Nurmi, L.; Ramo, V.; Harlin, A.; Ropponen, J. *Eur. Polym. J.* **2012**, *48*, 774.
12. Peng, B.; Hou, H. B.; Song, F. C.; Wu, L. B. *Ind. Eng. Chem. Res.* **2012**, *51*, 5190.
13. Rahaman, M. H.; Tsuji, H. *Macromol. React. Eng.* **2012**, *6*, 446.
14. Phuphuak, Y.; Chirachanchai, S. *Polymer* **2013**, *54*, 572.
15. Ren, H. X.; Ying, H. J.; Ouyang, P. K.; Xu, P.; Liu, J. *J. Mol. Catal. A: Chem.* **2013**, *366*, 22.
16. Marques, D. S.; Gil, M. H.; Baptista, C. *J. Appl. Polym. Sci.* **2013**, *128*, 2145.
17. Xiong, J. F.; Luo, S. H.; Wang, Q. F.; Wang, Z. Y.; Qi, J. *Des. Monomers Polym.* **2013**, *16*, 389.
18. Xiong, J. F.; Huo, J. P.; Peng, P.; Wang, Z. Y. *Adv. Mater. Res.* **2013**, *781–784*, 479.
19. Zhang, Y. J.; Lu, Y. B.; Guo, F.; Peng, C.; Li, M. M.; Xu, W. *J. Polym. Adv. Technol.* **2012**, *23*, 166.
20. Peng, P.; Xiong, J. F.; Li, B.; Mo, G. Z.; Cheng, R. H.; Wang, Z. Y. *Chin. J. Org. Chem.* **2013**, *33*, 1891.
21. Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **1998**, *31*, 2114.
22. Shaver, M. P.; Cameron, D. J. A. *Biomacromolecules* **2010**, *11*, 3673.
23. Perry, M. R.; Shaver, M. P. *Can. J. Chem.* **2011**, *89*, 499.
24. Lin, Y. L.; Zhang, A. Q.; Wang, L. S. *J. Appl. Polym. Sci.* **2012**, *124*, 4496.
25. Wang, Z. Y.; Zhao, H. J.; Wang, Q. F.; Ye, R. R.; Finlow, D. E. *J. Appl. Polym. Sci.* **2010**, *117*, 1405.
26. Luo, S. H.; Wang, Z. Y.; Mao, C. X.; Huo, J. P. *J. Polym. Res.* **2011**, *18*, 2093.
27. Wang, Z. Y.; Luo, Y. F.; Ye, R. R.; Song, X. M. *J. Polym. Res.* **2011**, *18*, 499.
28. Mao, C. X.; Luo, S. H.; Wang, Q. F.; Xiong, J. F.; Wang, Z. Y. *J. Appl. Polym. Sci.* **2012**, *155*, E339.
29. Mao, C. X.; Luo, S. H.; Wang, Q. F.; Xiong, J. F.; Wang, Z. Y. *Des. Monomers Polym.* **2012**, *15*, 575.
30. Takasu, A.; Narukawa, Y.; Hirabayashi, T. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 5247.

31. Moon, S. I.; Kimura, Y. *Polym. Int.* **2003**, *52*, 299.
32. Duan, J. F.; Du, J.; Zheng, Y. B. *J. Appl. Polym. Sci.* **2007**, *103*, 3585.
33. Orgueira, H. A.; Bueno, M.; Funes, J. L.; Galbis, J. A.; Varela, O. *J. Polym. Sci. Part A: Polym. Chem.* **1998**, *36*, 2741.
34. Fukushima, K.; Furuhashi, Y.; Sogo, K.; Miura, S.; Kimura, Y. *Macromol. Biosci.* **2005**, *5*, 21.
35. Chiosis, G.; Lucas, B.; Shtil, A.; Huezo, H.; Rosen, N. *Bioorg. Med. Chem.* **2002**, *10*, 3555.
36. Katritzky, A. R.; Aslan, D. C.; Leeming, P.; Steel, P. *J. Tetrahedron: Asymmetry* **1997**, *8*, 1491.
37. Reddy, V. M.; Reddy, K. R. *Chem. Pharm. Bull.* **2010**, *58*, 1081.
38. Thakuria, H.; Das, G. *Arkivoc* **2008**, 321.
39. Mamada, M.; Pérez-Bolívar, C.; Anzenbacher, P. *J. Org. Lett.* **2011**, *13*, 4882.
40. Wang, Z. Y.; Hou, X. N.; Mao, Z. Z.; Ye, R. R.; Mo, Y. Q.; David, E. F. *Iran. Polym. J.* **2008**, *17*, 791.
41. Ye, R. R.; Wang, Z. Y.; Luo, S. H.; Yang, L. T.; Xiao, X. *J. Appl. Polym. Sci.* **2011**, *121*, 420.
42. Ye, R. R.; Wang, Z. Y.; Wang, Q. F.; Yang, K.; Luo, S. H. *J. Appl. Polym. Sci.* **2011**, *121*, 3662.
43. Luo, S. H.; Wang, Q. F.; Xiong, J. F.; Wang, Z. Y. *J. Polym. Res.* **2012**, *19*, 9962.
44. Wang, Z. Y.; Zhao, Y. M.; Wang, F.; Wang, J. *J. Appl. Polym. Sci.* **2006**, *99*, 244.
45. Kim, E. S.; Kim, B. C.; Kim, S. H. *J. Polym. Sci. Part B: Polym. Phys.* **2004**, *42*, 939.
46. Luo, Y. F.; Wang, Z. Y.; Song, X. M.; Mao, Z. Z. *Prog. Chem.* **2008**, *20*, 1578.
47. Srisa-ard, M.; Baimark, Y. *J. Appl. Sci.* **2010**, *10*, 1937.
48. Yang, K. K.; Wang, X. L.; Wang, Y. Z.; Wu, B.; Jin, Y. D.; Yang, B. *Eur. Polym. J.* **2003**, *39*, 1567.
49. Zeng, J. B.; Li, Y. D.; Li, S. L.; Wang, Y. Z.; Yang, K. K. *J. Macromol. Sci. Part B: Phys.* **2009**, *48*, 635.
50. Cisek-Cicirko, I.; Lubczak, J. *J. Appl. Polym. Sci.* **2000**, *77*, 2667.