

Synthesis of Poly(lactic acid-co-menthol) via Direct Melt Polycondensation and Its Characterization

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ABSTRACT: Directly starting from D,L-lactic acid (LA) and L-menthol, poly(lactic acid-co-menthol) (PLAM) as potential solid mint flavor was synthesized via melt polycondensation. The synthetic conditions, including type and dosage of catalyst, temperature and time of copolymerization, were discussed. The structure and properties of the copolymer were systematically characterized with FTIR, ¹H-NMR, GPC, DSC, TG, and XRD. The influences of molar feed ratios on the properties of PLAM were

also discussed. The copolymer PLAM with the biggest M_w of 11,600 Da was obtained. The T_g of PLAM is lower than the T_g of homopolymer poly(D,L-lactic acid) (PDLLA), and all copolymers have higher thermal decomposition temperature. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: biodegradable; copolymerization; polycondensation; synthesis

INTRODUCTION

As the most familiar cool flavor, menthol has been widely used in many products, including daily chemicals, foods, tobacco products, medicines, and personal hygiene products due to its special advantages, such as good fresh cool, certain bactericidal effect, and cheapness.^{1–3} However, menthol has obvious deficiencies, including: (1) lower melting point (only about 42°C), easy sublimation or evaporation in the air, and not resisting high temperature, which make its applications limited in the fields requiring high temperature process, e.g., foods, cigarettes, and so on; (2) shorter and stronger instantaneous cool flavor, which makes the skin and the mouth uncomfortable or bitter, and affects the use of menthol in the food (e.g., chewing gum) and personal care products.^{4–6}

One of the ways to solve the above problems is to make menthol reacted into its derivatives and to make it be effective only when its derivatives is used. Mostly, the conversion method is the esterifi-

cation of menthol. Nowadays, for their excellent characteristics, such as refreshing, long-acting, pure cool flavor, and no bitterness, different menthol esters have been become an important class of new-type cool agents and extensively applied in many fields.⁷ It is noteworthy that these menthol esters derivatives are usually organic small molecules, and the loading of menthol with polymeric material by esterification is rarely reported before.

As an inexpensive natural metabolite with no side effects on the human body, lactic acid (LA) can be easily absorbed, and directly take part in the metabolism, promote digestion, suppress harmful intestinal bacteria, which make LA widely used in food industry. Currently, as safe food additives, LA and its derivatives can be used as acidifier, preservative, antioxidant, stabilizer, bread improver, emulsifier, moisturizers, nutrition enhancer, thickener, and so on.^{8,9} In cigarette industry, LA not only can keep the tobacco moisture, remove the impurities in tobacco, change the taste and improve tobacco quality, but also can reduce harmful ingredient by neutralization with nicotine.¹⁰

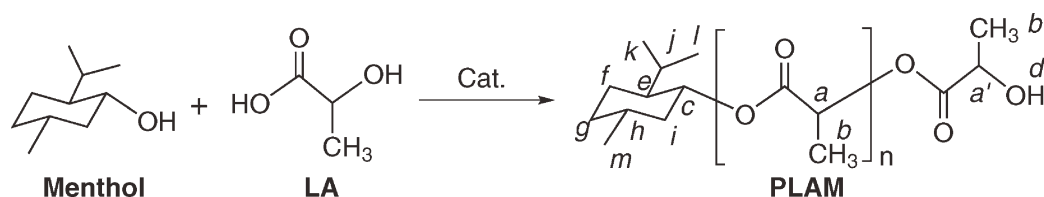
As a nontoxic, safe polymer derived from LA, biodegradable material polylactic acid (PLA) usually is used in biomedical fields, including surgical suture, bone fixation material, drug delivery carrier, and tissue engineering scaffold materials. For its good properties similar to common polymer materials, PLA is also an effective alternative to petroleum polymer. Therefore, there are more and more reports on the researches of PLA.^{11–13} However, there is no report on the modification of PLA by menthol.

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Scheme 1 The synthetic route of PLAM.

In these cases, we designed to synthesize a novel polymer poly(lactic acid-*co*-menthol) (PLAM) via the direct melt polycondensation of LA and menthol (Scheme 1). According to the design, once the polymer is degraded slowly, the function of the released LA and menthol may make PLAM a multifunctional additive in many fields, especially in the industries of food and tobacco. At the same time, as a preliminary investigation, the modified PLA were systematically characterized with FTIR, $^1\text{H-NMR}$, GPC, DSC, TG, and XRD in this article.

EXPERIMENTAL

Materials

D,L-Lactic acid (LA) was purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China), and L-menthol was purchased from J&K Scientific Ltd. (Beijing, China). All other chemicals, including *p*-toluenesulfonic acid (TSA), stannous chloride (SnCl_2), stannous oxide (SnO), zinc chloride (ZnCl_2), zinc oxide (ZnO), potassium hydrogen sulfate (KHSO_4), and ammonium iron(III) sulfate dodecahydrate [$\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] 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

The intrinsic viscosity ($[\eta]$) of the copolymer PLAM was determined with Ubbelohde viscometer (Cannon-Ubbelohde, State College, PA) using CHCl_3 as solvent at 25°C . The relative molecular weight and molecular weight distribution of the polymer were determined by gel permeation chromatography (Waters 1515 pump, Torrance, CA) with tetrahydrofuran as solvent at 35°C and a flow velocity 1 mL min^{-1} . Three Styragel HR columns from Japan covering a molecular weight range of 1×10^3 – 10^6 Da were used and calibrated using five polystyrene narrow standards from BF Goodrich (Richfield, OH). Molecular weight distributions for the samples were calculated using the Millennium 2010 software from Waters and were reported as polystyrene equivalent values.

IR spectra were obtained from an FTIR spectrometer (Bruker Vector 33, Ettlingen, Germany) by the

KBr salt slice method. $^1\text{H-NMR}$ spectra were recorded with a Varian NMR system 400 MHz (USA) with $\text{DMSO-}d_6$ as the solvent and TMS as internal standard. With a wavelength of $1.5406 \times 10^{-10}\text{ m}$ and a scanning scope of 2θ from 5° to 50° with $\text{Cu K}\alpha$ radiation, a Rigaku D/max-2000X X-ray diffractometer (Dandong, China) was used to investigate the crystallinity of the polymer.

The thermal properties of the polymer were measured by differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) with a PerkinElmer DSC7 thermal analyzer (PerkinElmer, Cetus Instruments, Norwalk, CT). The samples for DSC measurements (an average weight of 4 mg) were scanned at a heating rate of $10^\circ\text{C min}^{-1}$ under a nitrogen atmosphere (flow velocity 20 mL min^{-1}), and then they were cooled to -50°C for 5 min and heated again to 200°C . TG were performed at a heating rate of $10^\circ\text{C min}^{-1}$ under a nitrogen atmosphere (flow velocity 20 mL min^{-1}) also.

Preparation of PLAM

According to the previous works on direct melt homo-/copolymerization of LA,^{13–17} LA and menthol should be prepolymerized before copolymerization. After LA and menthol were uniformly mixed as preplanned molar feed ratio, the mixture was directly dehydrated for 5 h at 140°C under 4000 Pa in a three-necked flask equipped with a mechanical stirring device and a thermometer. After prepolymerization, the selected catalyst was added as predetermined weight percentage of dehydrated reactants (wt %), then melt copolymerization was carried out at a certain temperature (140 – 180°C) and an absolute pressure of 70 Pa for 3–11 h. When the reaction finished, the crude product was dissolved in CHCl_3 . The filtrate was subsequently precipitated by CH_3OH . After drying *in vacuo* to constant weight, the simple purification ordinarily produced a white (or yellowish) powder. The yield was within the range of 20–57%, and in most cases it was above 40%.

RESULTS AND DISCUSSION

Using LA and menthol as starting materials, the copolymer PLAM with different molar feed ratios (LA/menthol = 15/1, 64/1, 128/1) were directly synthesized via melt copolycondensation after the

TABLE I
The Influences of Different Catalysts on the Viscosity of PLAM^a

Run	Catalysts	Appearance of product	Yield / %	$[\eta]/(\text{dL g}^{-1})$
1	SnCl ₂	White solid	33.6	0.76
2	SnO	White powder	49.2	0.54
3	ZnO	Yellowish solid	56.5	0.34
4	ZnCl ₂	Yellowish solid	56.5	0.44
5	TSA	Yellowish solid	60.6	0.54
6	KHSO ₄	Yellowish solid	41.2	0.42
7	NH ₄ Fe(SO ₄) ₂ ·12H ₂ O	Yellowish solid	46.1	0.34

^a All runs were polymerized with a polycondensation temperature of 140°C, a polycondensation time of 5 h, and catalyst quantity of 0.3 wt %.

synthetic conditions was discussed. The structure and properties of these PLAM were characterized by FTIR, ¹H-NMR, GPC, DSC, XRD, TG, and viscosity $[\eta]$ measurements.

Appropriate synthetic conditions

First, different catalysts were screened. When the direct melt copolycondensation was carried out for 5 h at 140°C, absolute pressure 70 Pa, with the catalyst quantity of 0.3 wt % and the molar feed ratio LA/menthol of 64/1, the influences of catalyst types on the $[\eta]$ of PLAM were shown in Table I. It can be observed that the reaction catalyzed by SnCl₂ gave higher $[\eta]$ than other familiar catalysts, such as SnO, ZnCl₂, ZnO, and TSA used in the direct melt homo-/copolymerization of LA.^{14–22} This further demonstrates that SnCl₂ usually gives the best effects for its good dispersability in the reaction system.^{18,23,24} Therefore, SnCl₂ was selected as the catalyst in the following experiments.

When the direct melt copolycondensation was carried out at 140°C and absolute pressure 70 Pa for 5 h with the molar feed ratio LA/menthol of 64/1, the influences of catalyst SnCl₂ dosage on the $[\eta]$ of

PLAM was shown in Figure 1. Obviously, the $[\eta]$ reached a maximum value when the weight percent of catalyst SnCl₂ quantity was 0.3 wt % of the prepolymer. Once the quantity was too small, the reaction was so insufficient after a certain time that the $[\eta]$ was not high. When the quantity of SnCl₂ was excessive, short-chain molecule was apt to be formed through the degradation of polymer, which also was catalyzed by the metal catalyst.^{15,25} Therefore, the suitable dosage of catalyst SnCl₂ was 0.3 wt %.

When the melt copolymerization was carried out respectively at different temperatures for 5 h under the conditions of the molar feed ratio LA/menthol of 64/1, absolute pressure 70 Pa, and catalyst SnCl₂ quantity 0.3 wt %, the $[\eta]$ of the resulting polymer was shown in Figure 2. It was obvious that, the appropriate higher temperature was advantageous to increase molecular chain of the copolymer. However, when the temperature was too high, the side reactions, such as thermal degradation, and oxidation markedly took place. Even when the temperature was 180°C, not only the lower $[\eta]$ was obtained, but also the color of the purified product became yellowish. Thus, the appropriate temperature should be 160°C.

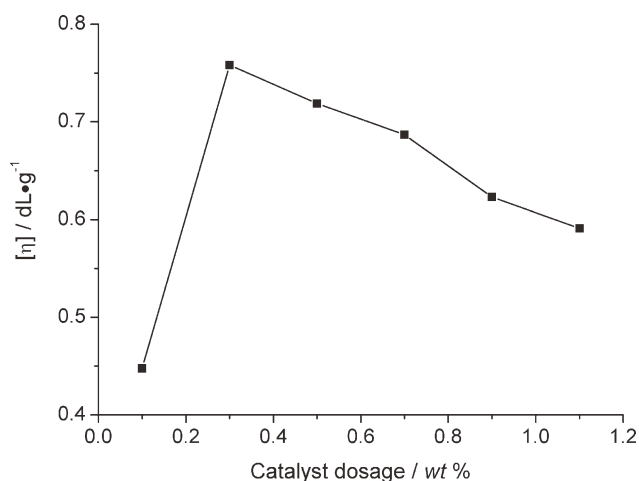


Figure 1 Influences of catalyst dosage on the viscosity of PLAM (conditions: 140°C, 5 h, and catalyst SnCl₂).

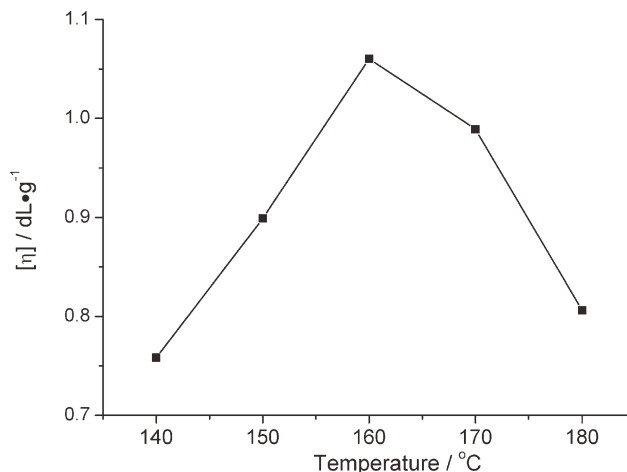


Figure 2 Influences of melt polymerization temperature on the viscosity of PLAM (conditions: 5 h, and catalyst SnCl₂ dosage 0.3 wt %).

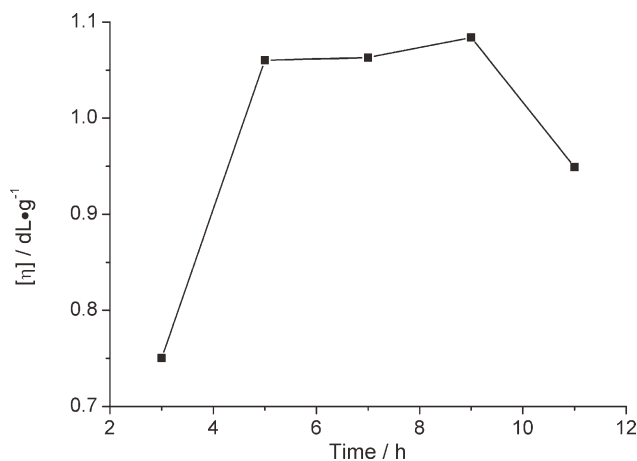


Figure 3 Influences of melt polymerization time on viscosity of PLAM (conditions: 160°C, and catalyst SnCl₂ dosage 0.3 wt %).

When the molar feed ratio LA/menthol was 64/1, the catalyst SnCl₂ quantity was 0.3 wt %, and the melt copolycondensation was carried out at 160°C and absolute pressure 70 Pa, the influences of the melt polymerization time on the $[\eta]$ of PLAM were shown in Figure 3. It was obvious that, the $[\eta]$ reached a maximum value after the reaction lasted for 9 h. When the time was too short, the polymerization was insufficient. However, once the reaction time was longer than 9 h, the oxidation and thermal degradation of polymer became serious. So, the $[\eta]$ dropped, the color of the purified product became deeper. Thus, the appropriate time may be 9 h.

Therefore, PLAM with different molecular weight could be obtained via the control of synthetic conditions. To get higher $[\eta]$, when the molar feed ratio LA/menthol was 64/1, the appropriate conditions for the synthesis of the copolymer PLAM via direct melt copolycondensation were as follows: catalyst SnCl₂ quantity 0.3 wt %, reaction temperature 160°C, absolute pressure 70 Pa, and reaction time 9 h. In this case, the maximum $[\eta]$ was 1.08 dL g⁻¹, and the corresponding weight-average molecular weight (M_w) was 8900 Da (Table II).

Structure characterization of PLAM

The structure of PLAM synthesized as the molar feed ratio LA/menthol 64/1 under the above appropriate synthetic condition was characterized with FTIR and ¹H-NMR spectroscopy. Compared with the homopolymer poly(D,L-lactic acid) (PDLLA) synthesized via direct melt polycondensation,¹⁴ it was elucidated that these compounds showed many similar absorptions in their FTIR spectra, e.g., the weak absorption of terminal OH group at 3511 cm⁻¹, the absorption of saturated C—H at 2993, 2953, 1456, and 1375 cm⁻¹, the strongest absorption of ester carbonyl near 1756 cm⁻¹, and the stronger absorption of C=O at 1276, 1189, and 1095 cm⁻¹. However, in FTIR of copolymer, peaks at 2925 and 2854 cm⁻¹ are observed (Fig. 4), whereas such peaks are absent in the homopolymer PLA. The absorption of saturated C—H (especially at the latter location) was led by CH₂ group¹⁵ in menthol ring.²⁶ This indicated that menthol segment has been introduced into the copolymer.

The structural studies on PLAM copolymers with different molar feed ratios by FTIR showed similar features at 3511 cm⁻¹. However, there are some differences in the strength of HO stretch vibration absorption for different molar feed ratios. In case of increasing LA content, the relative content of terminal OH became less, so its absorption strength became smaller. Contrarily, in case of increasing menthol content, the relative content of menthol became more, and the CH₂ absorption near 2854 cm⁻¹ became stronger obviously (Fig. 5).

The data of ¹H-NMR spectrum of PLAM synthesized as the molar feed ratio LA/menthol 64/1 were obtained as follows (Fig. 6). ¹H-NMR (CDCl₃ as solvent and TMS as internal reference), δ , ppm: 0.652–1.044 (H_{k-m} , CH₃ in menthol segment), 1.337–1.986 ($H_{b,b'}$, CH₃ in PLA segment, and other CH in menthol segment except H_{k-m} and H_c), 2.736 (H_d , terminal OH of PLA chain), 4.323–4.423 (H_a , CH in the terminal PLA segment), 4.635–4.805 (H_c , CH—O in menthol segment), 5.046–5.332 (m , H_b , CH in PLA chain). Especially, as a characteristic data of menthol's ester, the data of H_c is similar to the result in

TABLE II
The Influences of Molar Feed Ratios on Yield, $[\eta]$ and M_n of the Copolymers^a

Run	LA/menthol		Appearance of product	Yield (%)	$[\eta]$ (dL g ⁻¹)	M_{NMR} (Da ^b)	M_n (Da)	M_w (Da)	M_w/M_n
	Feed	Test ^b							
1	15/1	40/1	White solid	19.3	0.76	3100	2300	5600	2.43
2	64/1	90/1	White powder	29.9	1.08	6700	3600	8900	2.47
3	128/1	144/1	Yellowish solid	19.0	1.40	10,600	3600	11,600	3.22

^a All runs were polymerized with a polycondensation temperature of 160°C, a polycondensation time of 9 h, and catalyst SnCl₂ quantity of 0.3 wt %.

^b Tested by ¹H-NMR, and for M_{NMR} using 100 Da as unit.

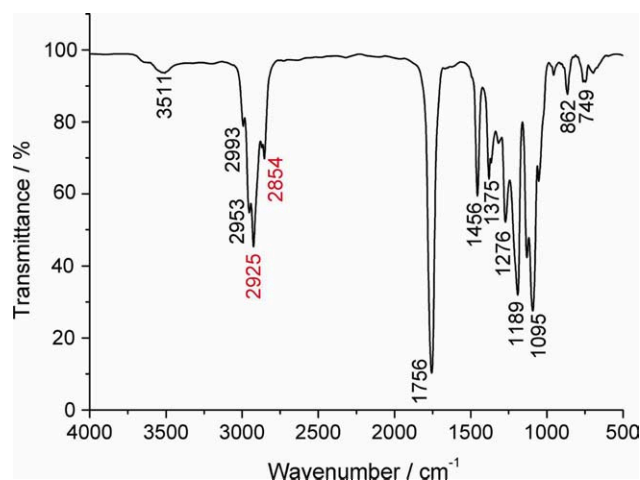


Figure 4 FTIR spectrum of PLAM synthesized as the molar feed ratio 64/1 (LA/menthol). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

literature.²⁷ Therefore, the data from FTIR and ¹H-NMR indicated that the direct melt copolycondensation of LA and menthol indeed gave the copolymer PLAM (Scheme 1).

According to the principle that the integral of proton peak area ratio reflects the amount of substance containing hydrogen group ratio, we could calculate the composition of the copolymer molar ratio of each unit using $S_{\text{Ha}+\text{Ha}'}/S_{\text{Hc}}$ as the standard (here, S is the integration area). The results of LA/menthol molar ratios were shown in Table II. It could be found that, the content of LA was higher than that

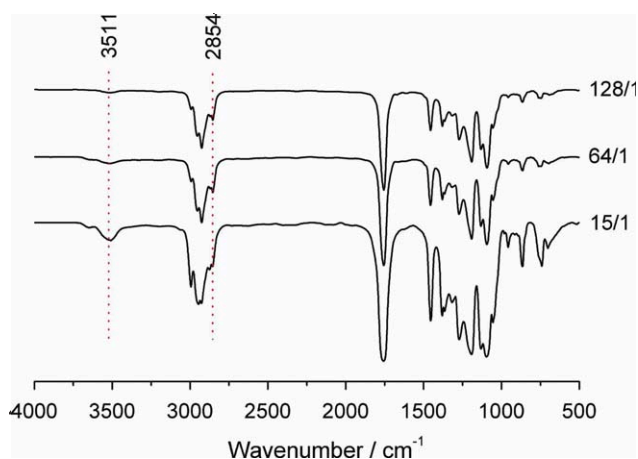


Figure 5 Infrared spectra of PLAM with different molar feed ratios (LA/menthol). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in the feed ratios. This may be related to the fact that, when LA escaped out of the reaction systems as lactide during the direct melt copolycondensation,^{13–17,28} the escape of menthol with higher escape rate also occurred.

Molecular weight of PLAM

The influences of different molar feed ratios on yield, $[\eta]$ and GPC results are shown in Table II. Obviously, with the increase of the molar feed ratio of LA, not only $[\eta]$ increased gradually, but also M_n , M_w , and PDI (M_w/M_n) had the trend of the

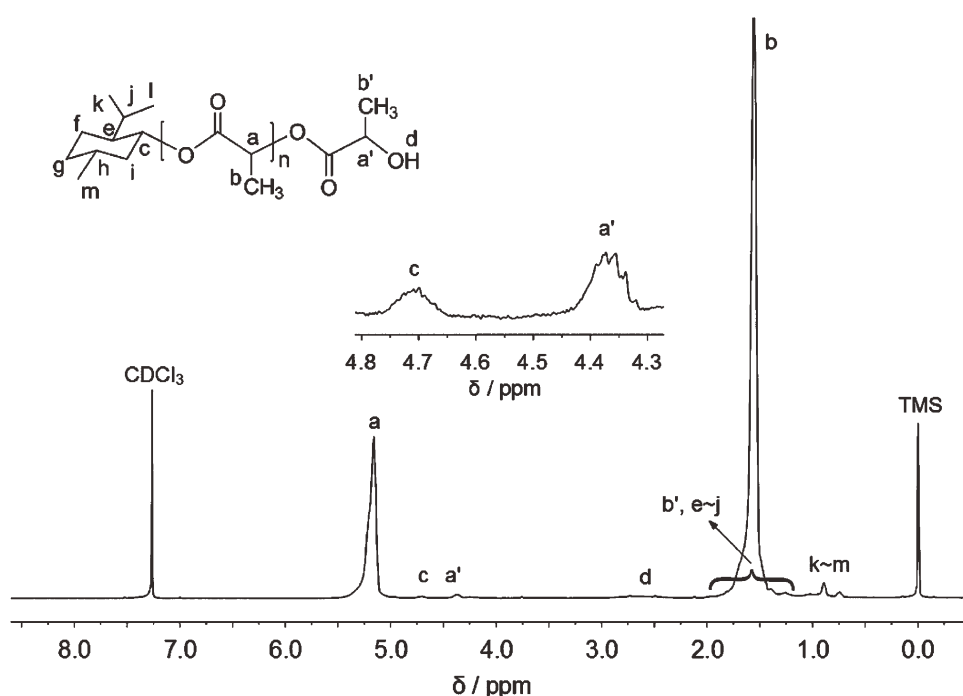


Figure 6 ¹H-NMR spectrum of PLAM synthesized as the molar feed ratio 64/1 (LA/menthol).

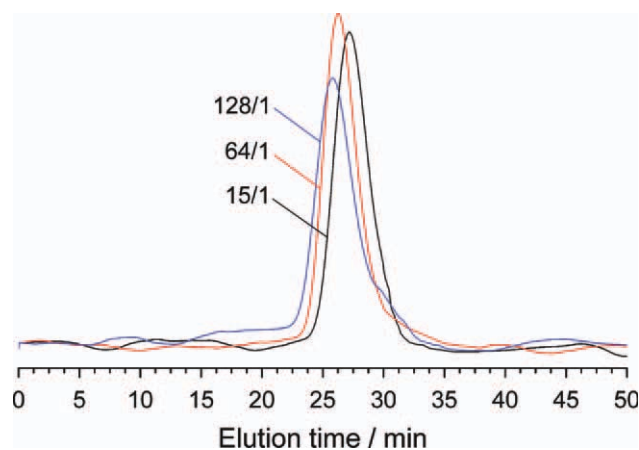


Figure 7 GPC curves of PLAM with different molar feed ratios (LA/menthol). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

corresponding increase. All the GPC flow curves only showed a single peak (Fig. 7), this also proved that the direct melt copolycondensation of LA and menthol indeed gave the copolymer PLAM. The PDI of the copolymers was above 2, though it is normal according to the Carothers' model, it is slightly higher than that reported before on the step-growth polymerization of LA,^{13–17} which may be related to the partial formation of ether bond between the OH terminal polymers.²⁸

At the same time, the minimum M_w of serial PLAM was 5600 Da in this study (Table II, Run 1). Generally, when the PLA biodegradable polymers were used as drug-delivery materials, the molecular weights were no more than 30,000 Da.^{14,29,30} As reported in the literatures,^{31–33} the PLAs material with molecular weight of 1800 Da could be applied in drug delivery, even PLA copolymers with molecular weight of only 900 Da could be used as drug-delivery device.

The molecular weight of PLAM synthesized here was overwhelmingly higher than 900 Da. Therefore, PLAM may be used as not only a potential solid mint flavor, but also an important biodegradable and functional drug carrier for its molecular weight meets the requirement for drug-delivery applications.

Thermal properties of PLAM

The influences of different molar feed ratios on the thermal properties of PLAM are shown in Table III. First, the DSC data showed that the glass transition temperature (T_g) of copolymers was lower than that of homopolymer PDLA synthesized via the direct melt polycondensation.¹⁴ At the same time, the data of the melting temperature (T_m) and heat were very limited in Table III, and the melting heat for the feed ratio LA/menthol of 15/1 was obviously smaller than that of PDLA. These indicated that the introduction of menthol made the structure changed. Especially, the decrease of structure regularity was advantageous for the movement of molecular chain, which was further demonstrated in the following analyses of XRD characterization.

On the other hand, the differential thermogravimetry (DTG) curves for the copolymers are shown in Figure 8. There were different single and acute thermal decomposition peaks for different molar feed ratios. These indicated that, once the thermal decomposition started, the entire polymeric chain instantaneously split into small molecular fragments.³⁴ Obviously, this weight loss only at certain higher temperature (e.g., when burning cigarettes) may be advantageous for the functional polymer PLAM to release menthol.

For different menthol esters, when they are used as the carriers of menthol, their data of decomposition temperature area from initial temperature (T_i) to final temperature (T_f) are crucial.^{35,36} The data in Table III showed that, the decomposition temperature of serial PLAM was higher than that of PDLA. More importantly, in our experiments, the data of maximum weight loss rate temperature (T_p) was between 250.8 and 266.5°C, which was similar to the reported data,³⁵ 253.2°C; and the weight loss range was from 232.1 to 293.6°C, which was also very similar to the results in literature,³⁶ 225.0–294.0°C. Therefore, PLAM may be a kind of effective solid mint flavor.

Usually, for only one hydroxyl-terminated PLA when its carboxyl was end-capped, the thermal degradation temperatures were found to be improved,

TABLE III
The Influences of Molar Feed Ratio on the Thermal Properties of PLAM^a

Run	LA/menthol	T_g (°C)	T_m (°C)	ΔH (J g ⁻¹)	T_i (°C)	T_f (°C)	T_p (°C)
1	15/1	30.2	122.6	4.02	253.5	290.2	266.5
2	64/1	39.2	ND ^b	ND ^b	232.1	274.0	250.8
3	128/1	38.6	ND ^b	ND ^b	250.8	293.6	265.9
PDLA ¹⁴		54.6	120.0	17.12	217.0	254.9	238.1

^a All runs were polymerized with a polycondensation temperature of 160°C, a polycondensation time of 9 h, and catalyst SnCl₂ quantity of 0.3 wt %.

^b Not detected.

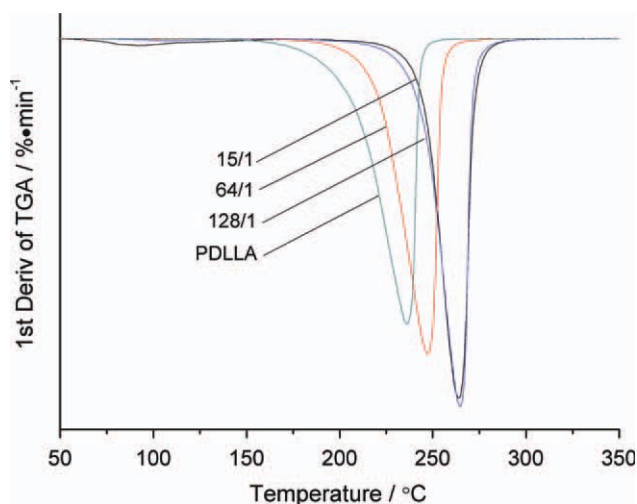


Figure 8 DTG curves of PLAM with different molar feed ratios (LA/menthol). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

compared to the neat PLA. However, this improve with the increase of the contents of modifying unit was not linear.³⁷ Herein, the thermal degradation temperatures may be controlled by two factors. First, the higher content of modifying agent menthol was advantageous for the higher thermal degradation temperature. Second, the higher molecular weight (Table II) was also beneficial to the higher thermal degradation temperature.³⁸ Therefore, when the molar feed ratio LA/menthol was 15/1 and 128/1, respectively, the thermal degradation temperature was similar each other, but both temperatures were higher than that of molar feed ratio of 64/1 (Table III).

Crystallinity of PLAM

The crystallinity of PLAs material is crucial for their physical and biological properties, especially degradability. The XRD results showed that PLAM is basically amorphous (Fig. 9, for LA/menthol 15/1, the copolymer was white viscous solid, so it was not tested with XRD). However, PDLLA synthesized via direct melt polycondensation was partially crystalline.¹⁴ Therefore, the XRD results further confirmed

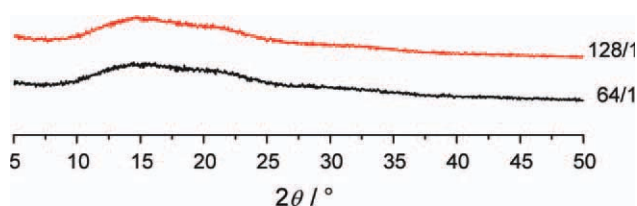


Figure 9 XRD spectra of PLAM with different molar feed ratios (LA/menthol). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that the introduction of menthol made the structure changed.

Fortunately, lower or no crystallinity is more beneficial for PLA biodegradable materials to be applied in the biomedical fields, especially drug delivery carrier materials, because there will be no residual microcrystalline after degradation *in vivo*.^{29,39}

CONCLUSION

Directly using D,L-LA and menthol as the starting materials, a novel biodegradable material PLAM was synthesized via melt polycondensation as designed for the first time. The structure and properties of the modified PLA by cool flavor menthol were systematically characterized with FTIR, ¹H-NMR, GPC, DSC, TG, and XRD. As a menthol polymeric ester, PLAM could be a potential solid mint flavor and biodegradable drug carrier, and its molecular weight could be controlled by synthetic conditions.

References

- Gupta, N.; Saxena, G. *Int J Pharm Bio Sci* 2010, 1, 715.
- Zheng, G. W.; Pan, J.; Yu, H. L.; Ngo-Thi, M. T.; Li, C. X.; Xu, J. H. *J Biotech* 2010, 150, 108.
- Faridi, U.; Sisodia, B. S.; Shukla, A. K.; Shukla, R. K.; Darokar, M. P.; Dwivedi, U. N.; Shasany, A. K. *Proteomics* 2011, 11, 2115.
- Sakata, I.; Iwamura, H. *Agric Biol Chem* 1979, 43, 307.
- Wu, Q. L.; Li, Q. Y.; Xiao, Y. J. *Flavor Fragrance Cosmetics* 2008, 6, 33.
- Chen, L.; Yan, R. A.; Du, S. X.; Huang, C. H.; Duan, H. Y.; Liu, Y. Q. *China Condiment* 2008, 33, 72.
- Xie, W. Y.; She, G. Q.; Feng, Z. M.; Nie, H.; Jiang, Y. Q. *China Surf Deterg Cosmetics* 2009, 39, 253.
- Qian, Z. L.; Hu, J.; Lei, Z. Z. *Ind Microbiol* 2001, 31, 49.
- Narayanan, N.; Roychoudhury, P. K. *Electron J Biotech* 2004, 7, 167.
- Wu, H. H. *J Northwest Univ Nationalities (Nat Sci)* 2010, 31, 67.
- Maharana, T.; Mohanty, B.; Negi, Y. S. *Prog Polym Sci* 2009, 34, 99.
- Rasal, R. M.; Janorkar, A. V.; Hirt, D. E. *Prog Polym Sci* 2010, 35, 338.
- Wang, Z. Y.; Luo, Y. F.; Ye, R. R.; Song, X. M. *J Polym Res* 2011, 18, 499.
- Zhao, Y. M.; Wang, Z. Y.; Yang, F. *J Appl Polym Sci* 2005, 97, 195.
- Wang, Z. Y.; Zhao, Y. M.; Wang, F.; Wang, J. *J Appl Polym Sci* 2006, 99, 244.
- Wang, Z. Y.; Zhao, H. J.; Wang, Q. F.; Ye, R. R.; Finlow, D. E. *J Appl Polym Sci* 2010, 117, 1405.
- Ye, R. R.; Wang, Z. Y.; Wang, Q. F.; Yang, K.; Luo, S. H. *J Appl Polym Sci* 2011, 121, 3662.
- Moon, S. I.; Kimura, Y. *Polym Int* 2003, 52, 299.
- Abe, H.; Tetsuka, H.; Doi, Y. *Polym Prepr Jpn* 2005, 54, 5243.
- Takasu, A.; Narukawa, Y.; Hirabayashi, T. *J Polym Sci A Polym Chem* 2006, 44, 5247.
- Lu, D. D.; Ren, Z. L.; Zhou, T. H.; Wang, S. F.; Lei, Z. Q. *J Appl Polym Sci* 2008, 107, 3638.
- Wei, Z. Y.; Liu, L.; Qu, C.; Liu, H. Z.; Qi, M. *J Funct Mater* 2010, 41, 656.

23. Moon, S. I.; Lee, C. W.; Miyamoto, M.; Kimura, Y. *J Polym Sci A Polym Chem* 2000, 38, 1673.
24. Moon, S. I.; Lee, C. W.; Taniguchi, I.; Miyamoto, M.; Kimura, Y. *Polymer* 2001, 42, 5059.
25. Duan, J. F.; Du, J.; Zheng, Y. B. *J Appl Polym Sci* 2007, 103, 3585.
26. Chen, Q. M.; Lu, Z. X.; Li, W. W.; Chen, X. Y.; Li, F. *Chem Bioeng* 2004, 21, 23.
27. Nakagawa, K.; Tomita, I. *Macromolecules* 2007, 40, 9212.
28. Luo, S. H.; Wang, Z. Y.; Mao, C. X.; Huo, J. P. *J Polym Res* 2011, 18, 2093.
29. Zhou, S. B.; Deng, X. M.; Li, X. H. *J Appl Polym Sci* 2004, 91, 1848.
30. Yang, F.; Song, F. L.; Pan, Y. F.; Wang, Z. Y.; Yang, Y. Q.; Zhao, Y. M.; Liang, S. Z.; Zhang, Y. M. *J Microencapsul* 2010, 27, 133.
31. Wang, Z. Y.; Hou, X. N.; Mao, Z. Z.; Ye, R. R.; Mo, Y. Q.; Finlow, D. E. *Iran Polym J* 2008, 17, 791.
32. Wang, N.; Wu, X. S.; Lujan-Upton, H.; Donahue E; Siddiqui A. *J Biomater Sci Polym Ed* 1997, 8, 905.
33. Wang, N.; Wu, X. S. *J Biomater Sci Polym Ed* 1998, 9, 75.
34. Apreutesei, D.; Lisa, G.; Hurduc, N.; Scutaru, D. *J Therm Anal Cal* 2006, 83, 335.
35. Yang, L.; Miao, M. M.; Wu, Y. Q.; Xiang, N. J. *Acta Tabacaria Sinica* 2008, 14, 1.
36. Liu, S. Y. Master Dissertation of Henan Agri Univ 2010, 39.
37. Lee, J. H.; Jeong, Y. G. *J Appl Polym Sci* 2010, 115, 1039.
38. Cam, D.; Marucci, M. *Polymer* 1997, 38, 1879.
39. Zhao, Y. M.; Wang, Z. Y.; Wang, J.; Mai, H. Z.; Yan, B.; Yang, F. *J Appl Polym Sci* 2004, 91, 2143.