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Synthesis and Characterization of a Novel Biomaterial: Maleic Anhydride-modified Poly(dl-lactic acid)

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Abstract: A novel modified poly(dl-lactic acid) (PDLLA) was obtained by covalently grafting of maleic anhydride onto the backbone of PDLLA, attempting to improve PDLLA's hydrophilicity and cell affinity and to provide reactive groups for further chemical modification. FTIR, ^{13}C NMR and DSC were used to characterize the maleic anhydride-modified PDLLA.

Keywords: Poly(dl-lactic acid), maleic anhydride, modification, characterization.

Weak hydrophilicity and cell affinity of poly(dl-lactic acid) (PDLLA) are important drawbacks to restrict its wide applications in medical areas despite its good biodegradability and biocompatibility[1, 2]. Chemical modifications are often used to overcome these drawbacks and some good results were obtained[3-7]. In this paper, we report the synthesis and characterization of a novel maleic anhydride-modified PDLLA (MPLA). The hydrolyzed maleic anhydride in MPLA could improve the hydrophilicity of PDLLA and therefore its cell affinity. Furthermore, the anhydrides could provide highly reactive groups for further chemical modification.

The maleic anhydride was grafted onto the backbone of PDLLA with viscosity-average molecular weight of 2200000, which was carried out at 100℃ for 10 h by melt free radical copolymerization using benzoyl peroxide (BPO) as an initiator (see **Scheme 1**). MPLA was purified by dissolving it in chloroform, and subsequently precipitating with excessive diethyl ether. The resulting fibrous solid was filtered and dried in vacuum at room temperature. FTIR, ^{13}C NMR and DSC were used for qualitatively characterizing MPLA and the acid-base titration for quantitative detection of the mass percentage of maleic anhydride in MPLA (grafting rate).

Results and Discussion

The number of glass transition temperatures (T_g) could reflect the purity of a polymer. The DSC curves of PDLLA and MPLA were detected by differential scanning calorimetry (DSC) on NETZSCH STA 449C thermal analyzer at a heating rate of 5℃/min from room temperature to 100℃ (showed in **Figure 1**). **Figure 1** indicates the glass transition peak

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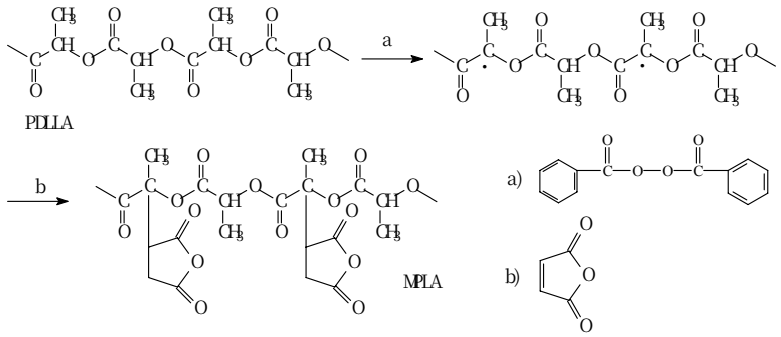
Scheme 1 Synthesis of MPLA from PDLLA and maleic anhydride



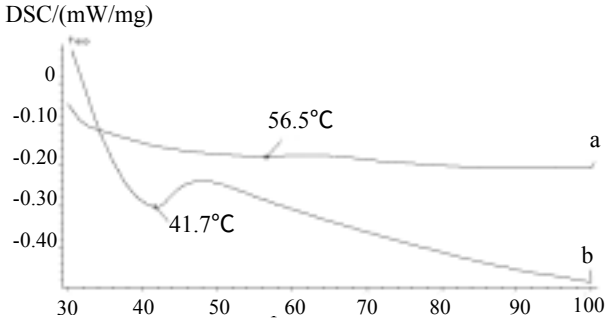
temperature ($T_{g,p}$) of 56.5℃ for PDLLA and 41.7℃ for MPLA. MPLA has a much different $T_{g,p}$ from that of PDLLA, exhibiting maleic anhydride moieties could reduce T_g of PDLLA.

Infrared (IR) spectra of PDLLA and MPLA were recorded on a Nicolet Magana-IR 550-Ⅱ Model spectrometer (**Figure 2**). Samples were film cast in THF onto transparent CaF_2 plates. The ^{13}C NMR spectra of PDLLA and MPLA were determined by AV 300 O NMR with $CDCl_3$ as the solvent and TMS as an internal standard (**Figure 3**).

IR spectrum can determine whether PDLLA had been modified with maleic anhydride or not. As shown in **Figure 2(c)**, at 1734cm^{-1}and 1773cm^{-1} exhibited a double peak, which is contributed by anhydride groups, indicating the existence of maleic anhydride in MPLA. The ^{13}C NMR spectrum of PDLLA (**Figure 3(a)**) indicated that there were three types of carbon in PDLLA (δ＝169.016-169.451 ppm, carbonyl carbon; δ ＝68.874-69.054 ppm, methine carbon; δ＝16.522-16.588 ppm, methyl carbon). Besides, there were another three new types of carbon (**Figure 3(b)**), which are assigned to anhydride carbons (δ ＝ 167.788 ppm), quarternary carbons (δ ＝ 72.311 ppm) and methylene carbons (δ＝25.557 ppm) in MPLA, respectively.

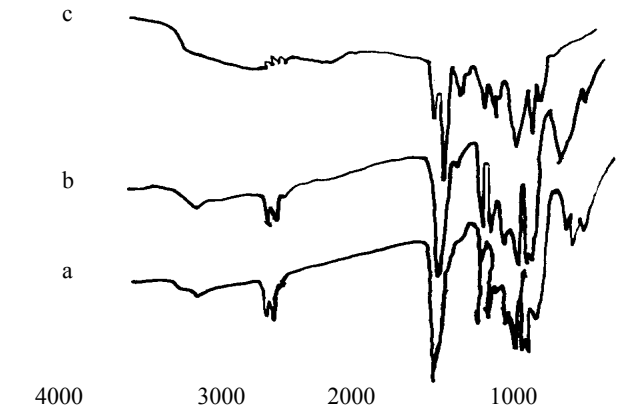
The results of acid-base titration indicated that the maleic anhydride grafting rates were 2.36% and 1.86%, respectively, when the fed mass of maleic anhydride were 10 and 5 percents of PDLLA.

Figure 1 DSC curves of PDLLA and MPLA



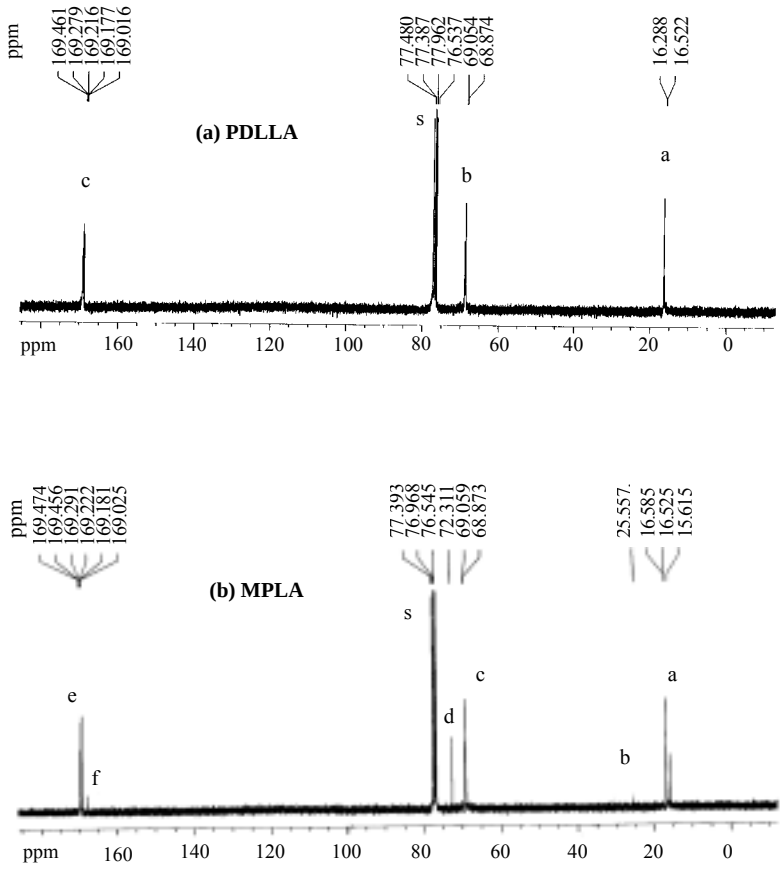
a. PDLLA; b. MPLA

Figure 2 IR Spectra of PDLLA and MPLA.



a. PDLLA; b. MPLA; c. subtracted IR spectrum of MPLA to PDLLA

Figure 3 13C NMR spectra of PDLLA and MPLA



The FTIR spectra, ^{13}C NMR spectra and acid-base titration revealed that maleic anhydride had been successfully introduced into the backbone of PDLLA. When the anhydrides in MPLA hydrolyze into carboxyl groups, the hydrophilicity and cell affinity of PDLLA could be substantially improved; furthermore, the anhydride groups provide highly reactive groups for further modification with aliphatic diamines, peptides or proteins, *etc*.

Acknowledgment

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