Cover sheet

Manuscript title

Carbon nanotube grafted poly(L-lactide)-block-poly(D-lactide) and its stereocomplexation with poly(lactide)s: the nucleation effect of carbon nanotube

Authors

Zhi-Qiang Cao, Xiao-Rong Sun, Rui-Ying Bao*, Wei Yang*, Bang-Hu Xie, Ming-Bo Yang

College of Polymer Science and Engineering, Sichuan University, State Key Laboratory of Polymer Materials Engineering, No.24 South Section 1, Yihuan Road, Chengdu , China, 610065

Total number of pages

8

Total number of figures

9

Total number of tables

1

*Corresponding authors. Tel/Fax: + 86 28 8546 0130. E-mail address: weiyang@scu.edu.cn (W. Yang) and baoruiying2005@126.com (RY Bao).

Supporting Information

Carbon nanotube grafted poly(L-lactide)-block-poly(D-lactide) and its stereocomplexation with poly(lactide)s: the nucleation effect of carbon nanotube

Zhi-Qiang Cao, Xiao-Rong Sun, Rui-Ying Bao*, Wei Yang*, Bang-Hu Xie, Ming-Bo Yang

College of Polymer Science and Engineering, Sichuan University, State Key Laboratory of Polymer Materials Engineering, No.24 South Section 1, Yihuan Road, Chengdu , China, 610065

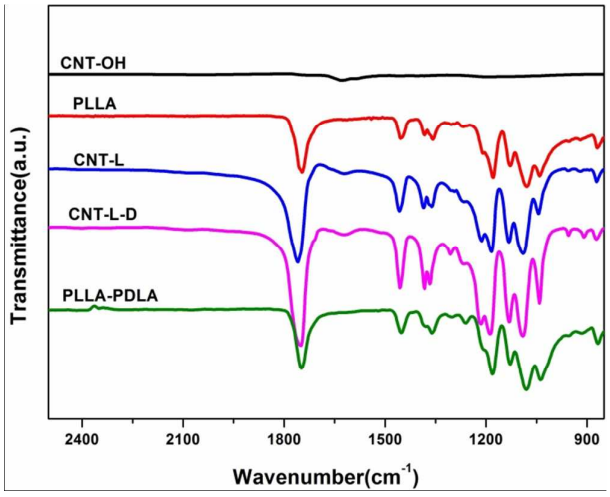


Figure S1. FTIR spectra of pristine CNT-OH, PLLA, CNT-L, CNT-L-D, and PLLA-PDLA.

As shown in Figure S1, the FTIR spectra of PLLA, CNT-L CNT-L-D, and PLLA-PDLA are very similar, and compared to the FTIR spectra of PLLA and PLLA-PDLA, an intense peak at around 1650 cm^{-1} presents for CNT-L and CNT-L-D, due to the introduction of CNT-OH. Both CNT-L-D and PLLA-PDLA exhibit characteristic absorption peak at around 908 cm^{-1} attributed to sc crystallites stretching vibration, demonstrating that PDLA was successfully grafted onto CNT-L.

*Corresponding authors. Tel/Fax: + 86 28 8546 0130. E-mail address: weiyang@scu.edu.cn (W. Yang) and baoruiying2005@126.com (RY Bao).

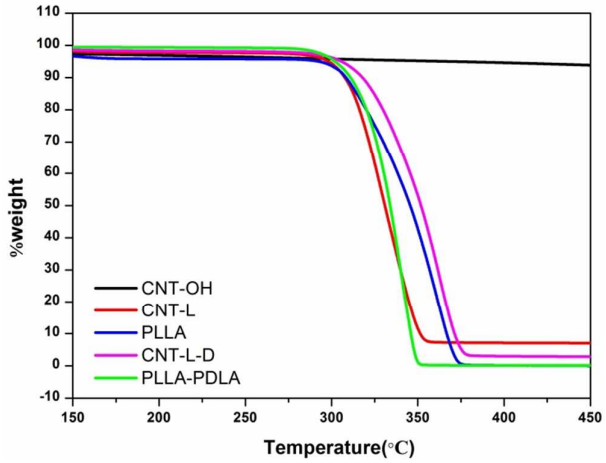


Figure S2. Comparison of TGA themograms among CNT-OH, PLLA, CNT-L, PLLA-PDLA and CNT-L-D.

Thermogravimetric analysis (TGA) was performed using a TA Instruments Q500 analyzer (USA) in a dry nitrogen atmosphere from 30 to 700 ℃ at a heating rate of 10 ℃/min. The amount of grafted PLLA and PLLA-PDLA chains on the MWCNT surface can be evaluated by the weight loss resulting from thermal degradation of PLLA and PLLA-PDLA during the heating process. Figure S2 shows the comparison of TGA thermograms among CNT-OH, PLLA, CNT-L, PLLA-PDLA and CNT-L-D. Notably, PLLA and PLLA-PDLA show a 100% weight loss in the temperature range of 250–450 °C due to the thermal decomposition of the PLLA and PLLA-PDLA chains, whereas the pristine MWCNT-OH reveals no appreciable weight loss during the heating process up to 450 ℃, which allows us to directly estimate the amount of the grafted chains in the nanohybrids using the weight loss recorded at 450 ℃. CNT-L nanohybrid shows the major weight loss (about 92.5%) in the temperature range of 250–450 °C due to the thermal decomposition of the grafted PLLA chains. The grafted amount increases to be as high as 96.4 wt% in the CNT-L-D nanohybrid with further formation of PDLA block. The content of carbon nanotubes is 3.6%wt in CNT-L-D, and 7.5%wt in CNT-L. According to the hydroxyl group content of carbon nanotubes and Mn of grafted PLA tested

by NMR, it is estimated that about 50% hydroxyl group on carbon nanotubes take part in initiating L-lactide ring-opening polymerization.

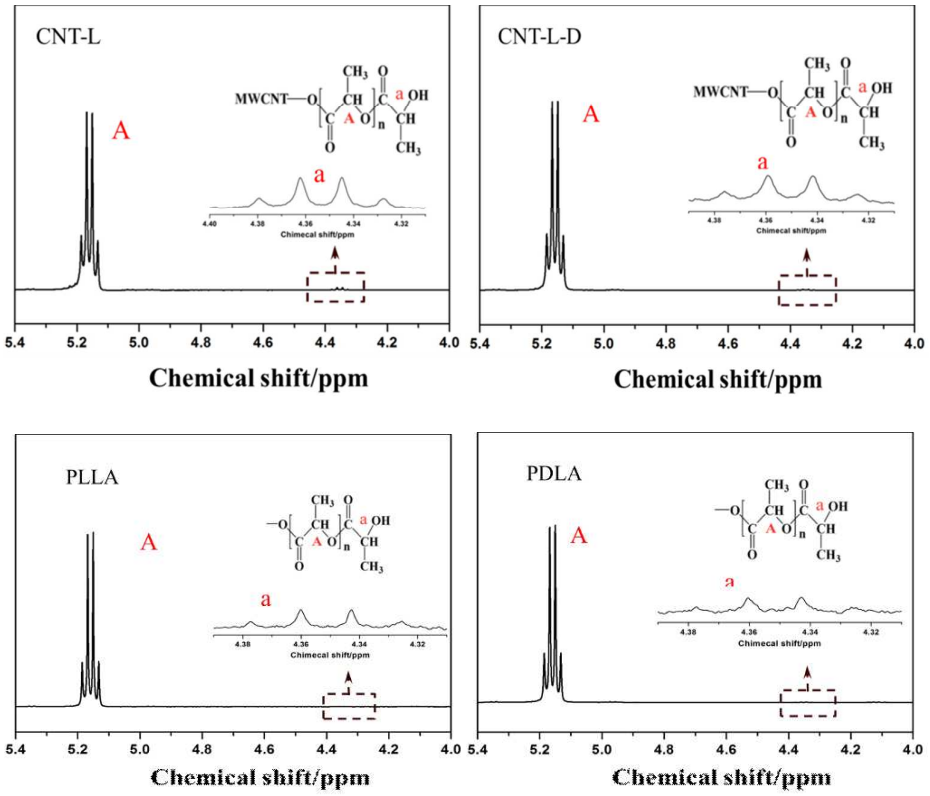


Figure S3. ^{1}H NMR spectra of CNT-L, CNT-L-D, PLLA and PDLA.

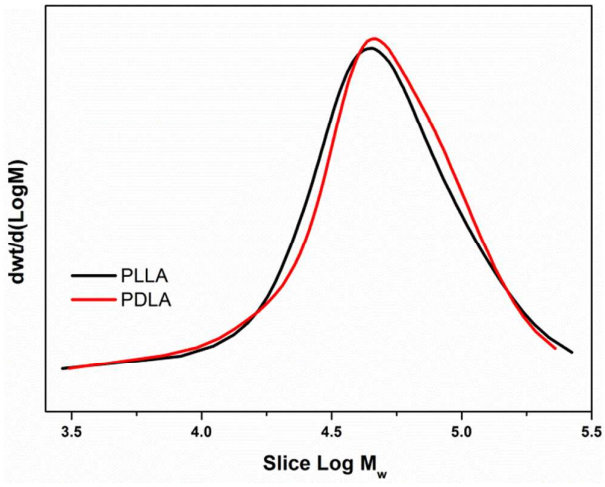


Figure S4. GPC curves for PLLA and PDLA.

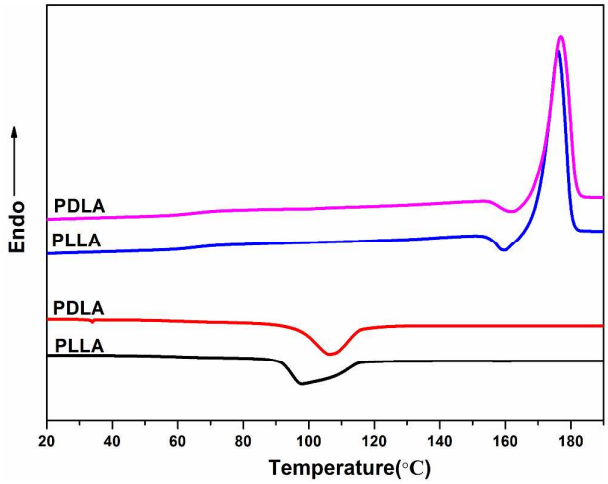


Figure S5. DSC crystallization curves (5 °C/min) and the subsequent melting (10 °C /min) curves of PLLA and PDLA after holding at 200 °C for 3 min.

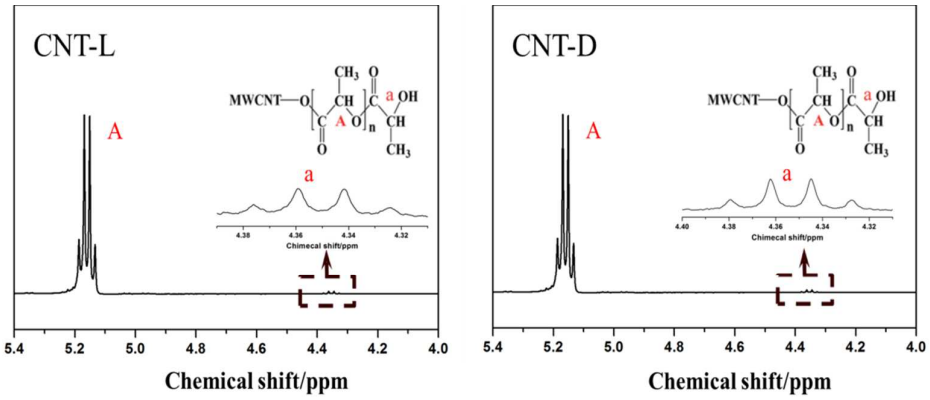


Figure S6. 1H NMR spectra of CNT-L and CNT-D.

Table S1. The molecular weight of the as-synthesized CNT-L, CNT-D from H NMR.

	CNT-L	CNT-D
M_n (g mol-1)	7.56×10^3	7.62×10^3

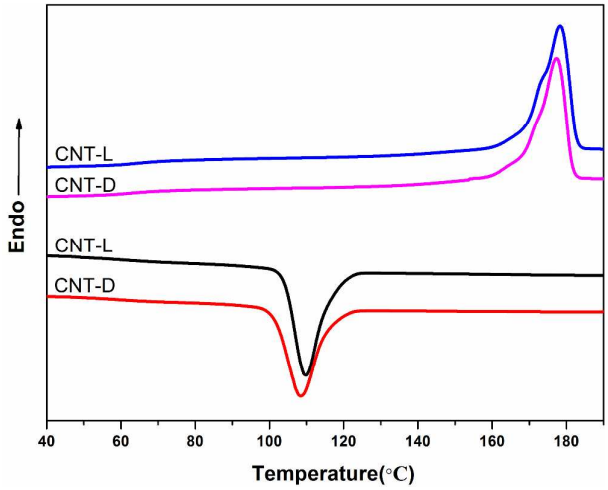


Figure S7. DSC crystallization curves (10 °C/min) and the subsequent melting (10 °C /min) curves of PLLA and PDLA after holding at 200 °C for 3 min.

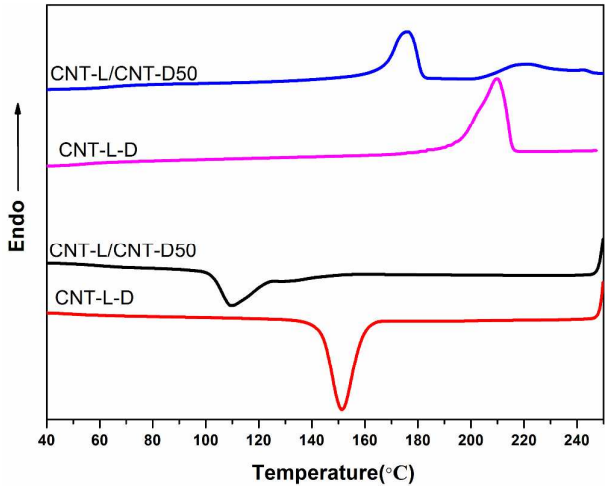
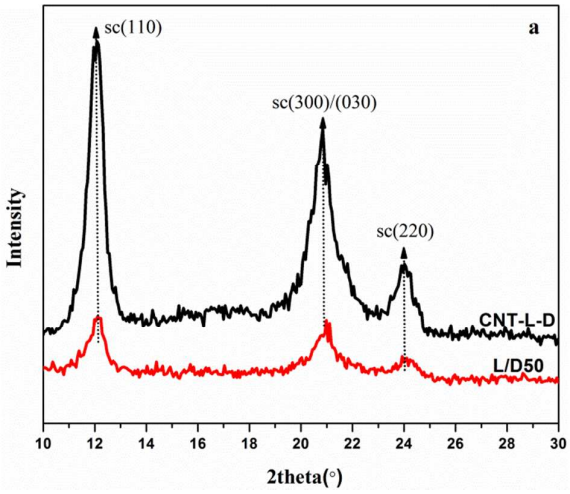


Figure S8. DSC crystallization curves (10 °C/min) and the subsequent melting (10 °C /min) curves of CNT-L-D and CNT-L/CNT-D50 after holding at 250 °C for 3 min.

In the first step of synthesis of CNT-L, there is no guarantee that all –OH groups on the surface of CNT can initiate L-lactide ring-opening polymerization to form "long-chain" of PLLA. It is possible that there are a few free –OH groups unreacted for some reasons. In the second step of synthesis of block copolymer CNT-L-D, due to the steric effect, it is more difficult for these left free -OH groups unreacted in the synthesis of CNT-L on the surface of CNT to initiate D-lactide

ring-opening polymerization, so the possibility of D-LA reacting with the left free -OH groups on the surface of CNT directly should be very low, leading to much greater possibility that D-LA grafts onto the end -OH groups in the grafted PLLA chains.

We also synthesized CNT-g-PDLA, which has similar molecular weight and crystallization behavior with CNT-g-PLLA, as shown in Figure S 6-7 and Table S1. The equal mass ratio blend of CNT-g-PDLA and CNT-g-PLLA cannot form exclusive sc crystallites during melt crystallization, however the synthesized block copolymer CNT-L-D can form exclusive sc crystallites during melt crystallization as shown in Figure S8, which is similar to liner poly(L-lactide)-block-poly(D-lactide). These results indicate that the CNT-L-D was synthesized successfully.



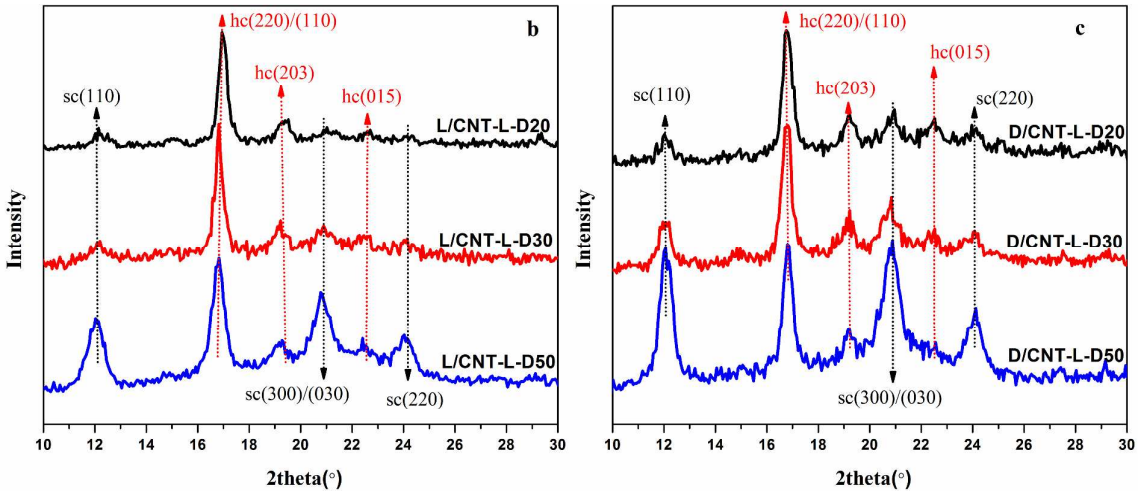


Figure S9. WAXD patterns of solution cast (a) CNT-L-D and L/D50 blend, (b) L/CNT-L-D, and (c) D/CNT-L-D blends with different CNT-L-D contents.