Biocompatible and biodegradable ultrafine fibrillar scaffold materials for tissue engineering by facile grafting of L-lactide onto chitosan

Supporting information

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Degree of deacetylation. %DD of used chitosans was estimated using two methods; the first one is based on the weighted ratio of surface area of methyl protons of acetylated amine (peak CH_3, fig S1) to glucosamine ring protons.[1, 2] For chitosans with intermediate %DD values, it can be estimated by integrating just acetal peaks of glucosamine and acetylglucosamine units (1 and 1', respectively). In our case both methods gave satisfactory results (method I and II, respectively in Table 1).

Table 1. Degree of deacetylation of chitosans, based on ^{1}H NMR spectra (fig. S1).

	%DD	
	method I	method II
	$\%DD = \left\{1 - (\frac{1}{3} I_{CH3} / \frac{1}{6} I_{H2-H6})\right\} \times 100$	$\%DD = \left\{I_{H1'} / \left(I_{H1} + I_{H1'}\right)\right\} \times 100$
HMWCHIT	79.4	80.0
LMWCHIT	81.5	80.2

Table 2. Solubility of HMWCHIT based samples. Typically 10-15 mg of each sample was dissolved in 1.0 mL of solvent and kept at room temperature for 24 hours. Dipole moment of each solvent is provided.

CHIT-PLA ratio	Solvent/Dipole moment										
	DMSO DMF	AcN[a]	Acetone MEK	Ethyl acetate	AcOH glacial	THF	CH_2Cl_3 $CHCl_3$	t-BuOH EtOH	ether	CCl_4	Benzene Toluene
	3.96 3.82	3.92	2.88 2.78	1.78	1.76	1.63	1.60 1.15	1.69	1.15	0.00	0.00 0.36
1 : 4[b]	+	+	+	+	+	+	+	×	p	×	×
1 : 6[b]	+	+	+	+	+	+	+	×	p	×	p
1 : 12	+	+	+	+	+	+	+	×	p	×	+
1 : 18	+	+	+	+	+	+	+	×	p	×	+
1 : 24	+	+	+	+	+	+	+	×	p	×	+

Legend:
+ – fully soluble;
p – partially soluble, most probably low molecular fraction;
× – insoluble.

a) acetonitrile;
b) both samples were soluble in 1,1,1,3,3,3-hexafluoro-2-propanol and 1,1,1-trifluoroethanol;

Figure S1. ^{1}H NMR spectra of high (HMWCHIT) and low (LMWCHIT) molecular weight chitosans used for L-lactide grafting.

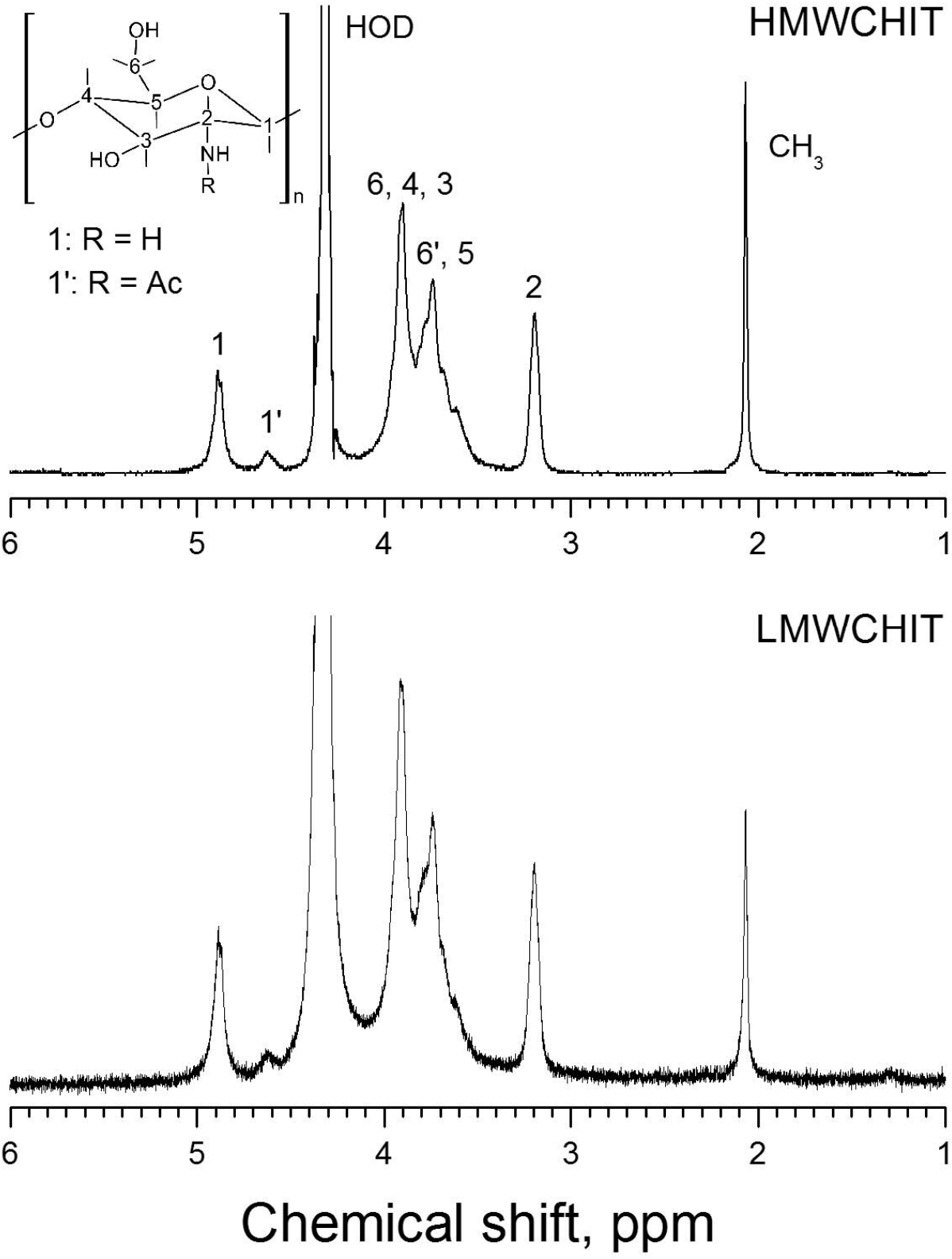


Figure S2. FTIR spectra of chitosans used for L-lactide grafting and polylactic acid (M_W=175 kDa). Spectra of chitosans were collected using pellet method by dispersing of 20.0 mg of dried chitosan in 180.0 mg of KBr (10% w/w). PLA spectrum was recorded using 1% (w/w) solution in chloroform (solvent spectrum subtracted).

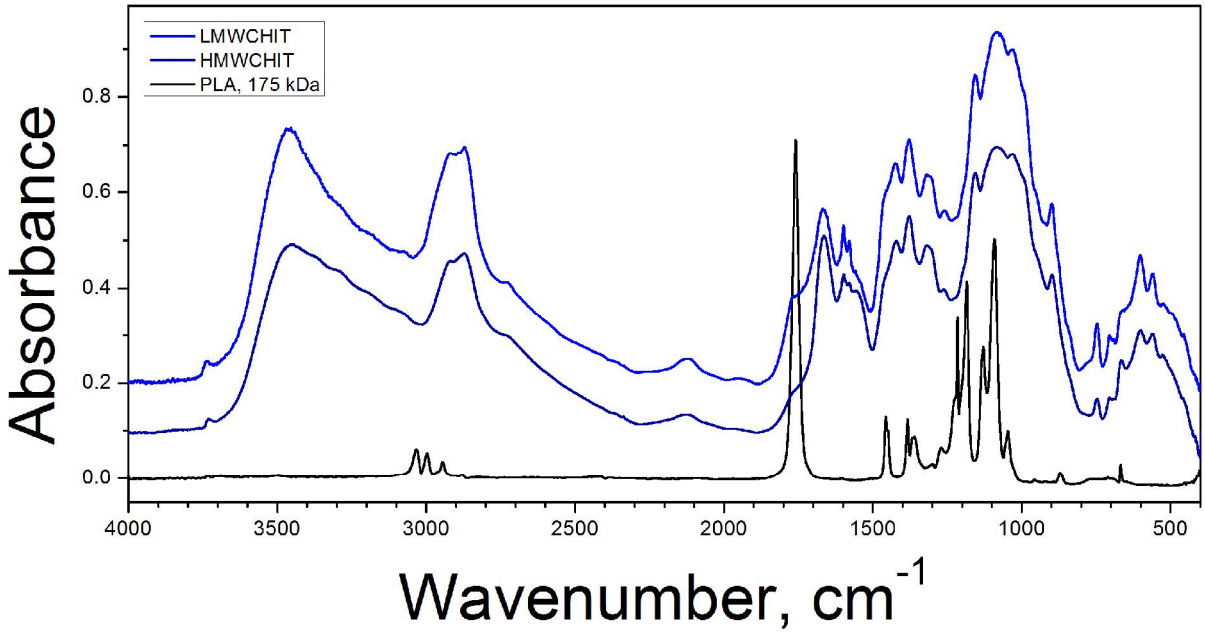


Figure S3. HMQC spectrum of HMWCHIT-PLA 1:6 sample in d_6-DMSO, after 3 hours of reaction at 40 °C.

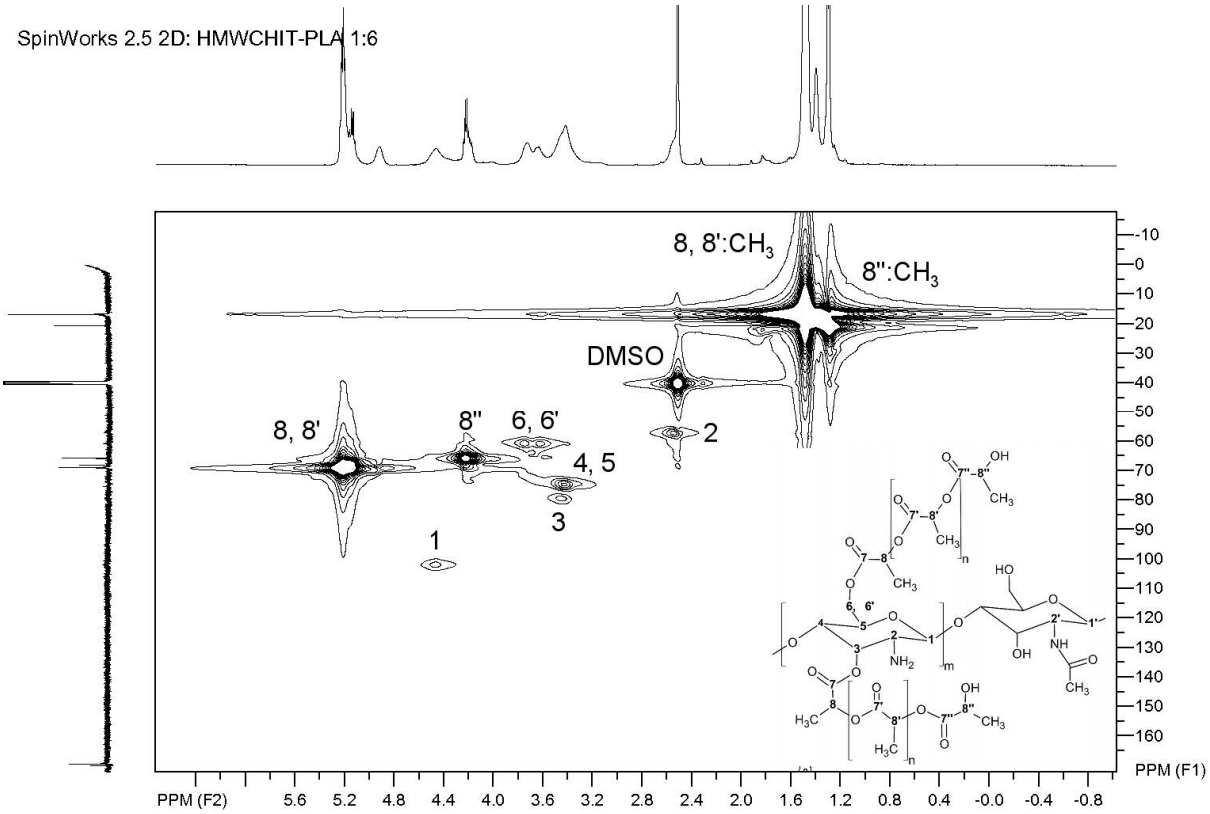
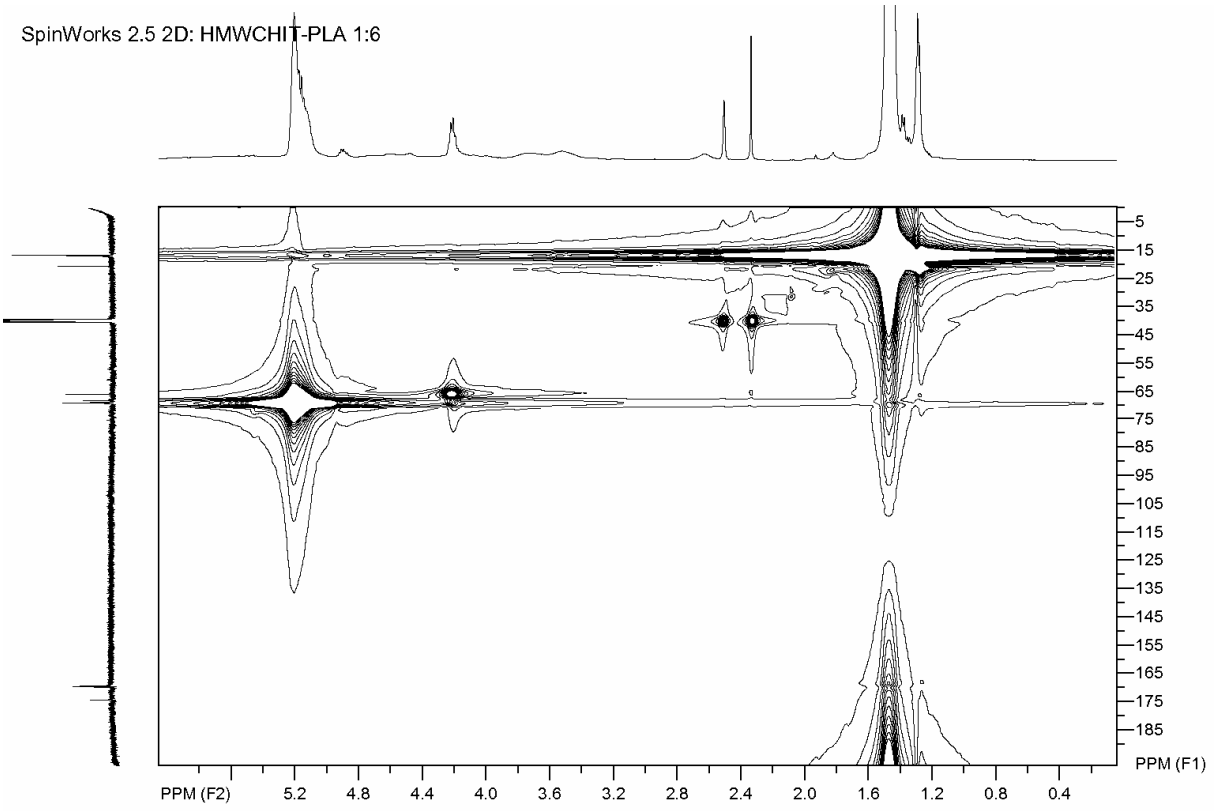


Figure S4. HMQC spectrum of HMWCHIT-PLA 1:6 sample, after 4 hours of reaction at 40 °C. Peak assignments are the same as on Fig. S3.



References

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