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Reply to Letter to the Editor

Dear Editor,

We would like to thank Dr Skotak and co-workers for their helpful comments regarding the paper published as *Carbohydrate Polymers*, 80 (2010), 499–504. On behalf of Honglin Chen, Jin Huang, Jiahui Yu, Shiyuan Liu, Daxin Wang, Yaping Li and myself, the authors of the paper "One-step synthesis of amino-reserved chitosan-graft-polycaprolactone as a promising substance of biomaterial, *Carbohydrate Polymers*, 80 (2010), 499–504", it's my pleasure to discuss some of the questions mentioned in their letter.

Chitosan and PCL are good and important candidates as biomaterials. It is still our joint goal to combine their good characteristics to yield novel biomaterials used as drug carriers, tissue engineering materials and imagine agents. It was fortuitous that Dr Skotak and colleagues reported the facile approach to synthesize the graft copolymer of chitosan-graft-polylactide. We initially repeated this research work, and synthesized the graft copolymer of chitosan-graft-polylactide using the method described in the paper "Biocompatible and Biodegradable Ultrafine Fibrillar Scaffold Materials for Tissue Engineering by Facile Grafting of L-Lactide onto Chitosan", *Biomacromolecules*, 9 (2008), 1902–1908. With the inspiration of the synthesis method of chitosan-graft-polylactide, we attempted to synthesize another graft copolymer of chitosan-graft-polycaprolactone, and published the experimental results in *Carbohydrate Polymers*, 80 (2010), 499–504. Although we cited the earlier research work, there were some omissions in our paper, including the failure to directly acknowledge the source of the sentence "the buffering properties of the monobasic phosphate ion avoid rapid and uncontrolled pH changes during the quenching of the reaction". We are very sorry not to cite this paper again directly after this sentence. We also appreciate deeply Dr Skotak and colleagues' research and useful comments about our paper.

Actually, it is difficult to purify the chitosan-graft-polycaprolactone copolymer. So we reprecipitated it several times to remove the PCL homopolymers. The salts including methanesulfonic acid were removed by several washings with water and subsequent dialyzing at low temperature to avoid the degradation of PCL. The resultant copolymers showed no measurable fluorescence, which suggested that there was no methanesulfonic acid/salt in the products. So it was thought that the graft copolymer of chitosan-graft-polycaprolactone was sufficiently pure.

Regarding the ^{1}H NMR spectrum presented in Fig. 2 for the CS-g-PCL (1:12) sample, the proton peaks of glucosamine monomeric unit marked as 3, 4, 5, 6, and 6′ have higher intensities than those of the methylene protons of PCL sidechains. We thought that the peak marked as 3, 4, 5, 6, and 6′ was the chemical shift of five protons of glucosamine monomeric unit, whereas the peak marked as α or γ was the chemical shift of two protons of PCL

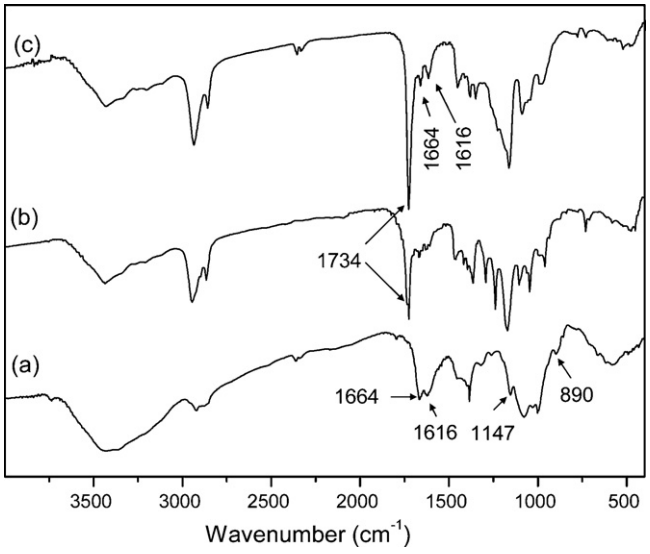

Fig. 3. FT-IR spectra of (a) CS; (b) PCL and (c) CS-g-PCL (1:12).

sidechains. Average number of ε-CL units per glucosamine unit in CS, $CL_n = A_{[(\alpha)/2]}/A_{[(3,4,5,6,6')/5]}$, were calculated from ^{1}H NMR, which was also described in the paper published in *Journal of Polymer Science: Part A: Polymer Chemistry*, 44 (2006), 5353–5361. The integral errors of NMR peaks resulted in the errors of the CL_n. We accept a better approach would be to use the ratio of integrals of terminal (ε′) to internal (ε) methylene protons to calculate the average chain length of oligomeric PCL dangling group. We tried to assign the peaks of ^{1}H and ^{13}C NMR according to the papers published in *Biopolymers*, 83 (2006), 233–242, *Journal of Polymer Science: Part A: Polymer Chemistry*, 45 (2007), 2556–2568 and *Biopolymers*, 78 (2005), 163–170, respectively. These papers were cited in the corresponding paragraph of our paper. We do appreciate your 2D NMR spectrum about the sample labeled as GluN-CL 1:12, which is very helpful to this current work and our future work.

The order of CS-g-PCL(1:6) < CS-g-PCL(1:8) < CS-g-PCL(1:24) < CS-g-PCL(1:12) was ranked according to their cell viability in our paper. It was thought that there were lots of factors that led to the cytotoxicity. The explanation about the cytotoxicity of chitosan-graft-polycaprolactone is appreciated. It was thought that the *in vitro* cytotoxicity of material was not a key factor when used as biomaterial. So we only showed the results of the cytotoxicity of chitosan-graft-polycaprolactone. The detail results including the possible reasons about the *in vivo* toxicity of chitosan-graft-polycaprolactone used as antitumor drug (SN-38) carrier is being explored in our group.

Here we attached the original FT IR spectra of (a) CS, (b) PCL and (c) CS-g-PCL. We appreciate pointing out our mistakes in the FT-IR

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spectra. The malposition of the spectra of CS and CS-g-PCL resulted from the malposition of their horizontal ordinates. We will submit the correct FT IR spectra of (a) CS, (b) PCL and (c) CS-g-PCL which can be considered as a revised material of our paper (Fig. 3).

Finally, the useful advice about our paper is appreciated.

Your sincerely,

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