# Supporting Information for Wrapping Amino-bearing Block Copolymer Cylinders around Carboxyl-bearing Nanofibers: A Case of Hierarchical Assembly

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**PDMAEMA nanofibers stained with Methyl Iodide.** As shown in Figure S1, the PDMAEMA fibers were stained with methyl iodide overnight and characterized by TEM analysis. The fibers had a uniform gray layer outside of a light core, indicating that the PDMAEMA chains were uniformly distributed on the outside layer.

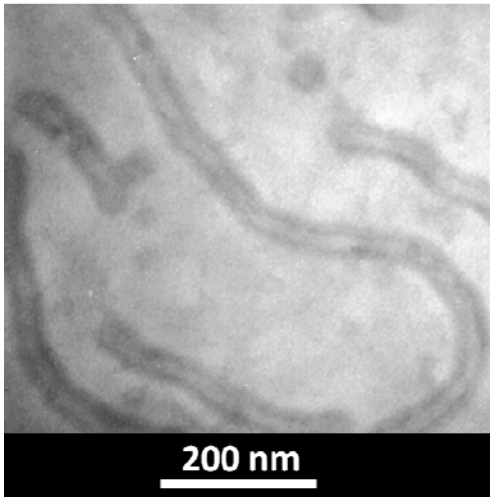


**Figure S1.** TEM images of PDMAEMA fibers stained with Methyl Iodide.

**$^1$H NMR Analysis of the PDMAEMA Fibers and Complex Micelles.** The ANCs were photo-crosslinked in order to lock their morphology, and they were then collected by ultra-centrifugation from their methanol dispersions. The x-ANCs were then re-dispersed into $d_5$-pyridine and collected by ultra-centrifugation again. These two steps were repeated once more to complete the solvent switching. Similar

procedures were used to obtain $d_5$-pyridine dispersions of the composite nanofibers. After solvent switching, the micelles were dispersed by stirring before $^1$H NMR analysis. The sample of complex micelles used was the same as that shown in Figure 4c.

By comparing the $^1$H NMR spectra shown in Figure S2, three observations were made. Firstly, at the polymer stage, all the peaks corresponding to the triblock copolymer were visible. Secondly, after cylindrical micelles were formed and they were crosslinked, the peaks corresponding to the PCEMA-core disappeared, but the peaks of the PDMAEMA and PtBA blocks were still clearly visible. Thirdly, after the formation of core-shell composite nanofibers, all of the peaks of the PDMAEMA block had disappeared as well. The disappearance of PCEMA peaks after crosslinking is understandable, because once the PCEMA block was crosslinked, it was no longer soluble, and thus should not generate any $^1$H NMR signals.[1, 2] The complete disappearance of the PDMAEMA peaks suggests that most of the PDMAEMA chains, if not all of them, were distributed inside the shell of the complex micelles. Because they were isolated from their surroundings by the crosslinked PCEMA shell, the signal of the interior PDMAEMA chains were no longer detectable.[2] This is illustrated in Scheme 2c, as most of the PDMAEMA chains are distributed inside the PCEMA shell but the PtBA chains are distributed both inside and outside the shell.

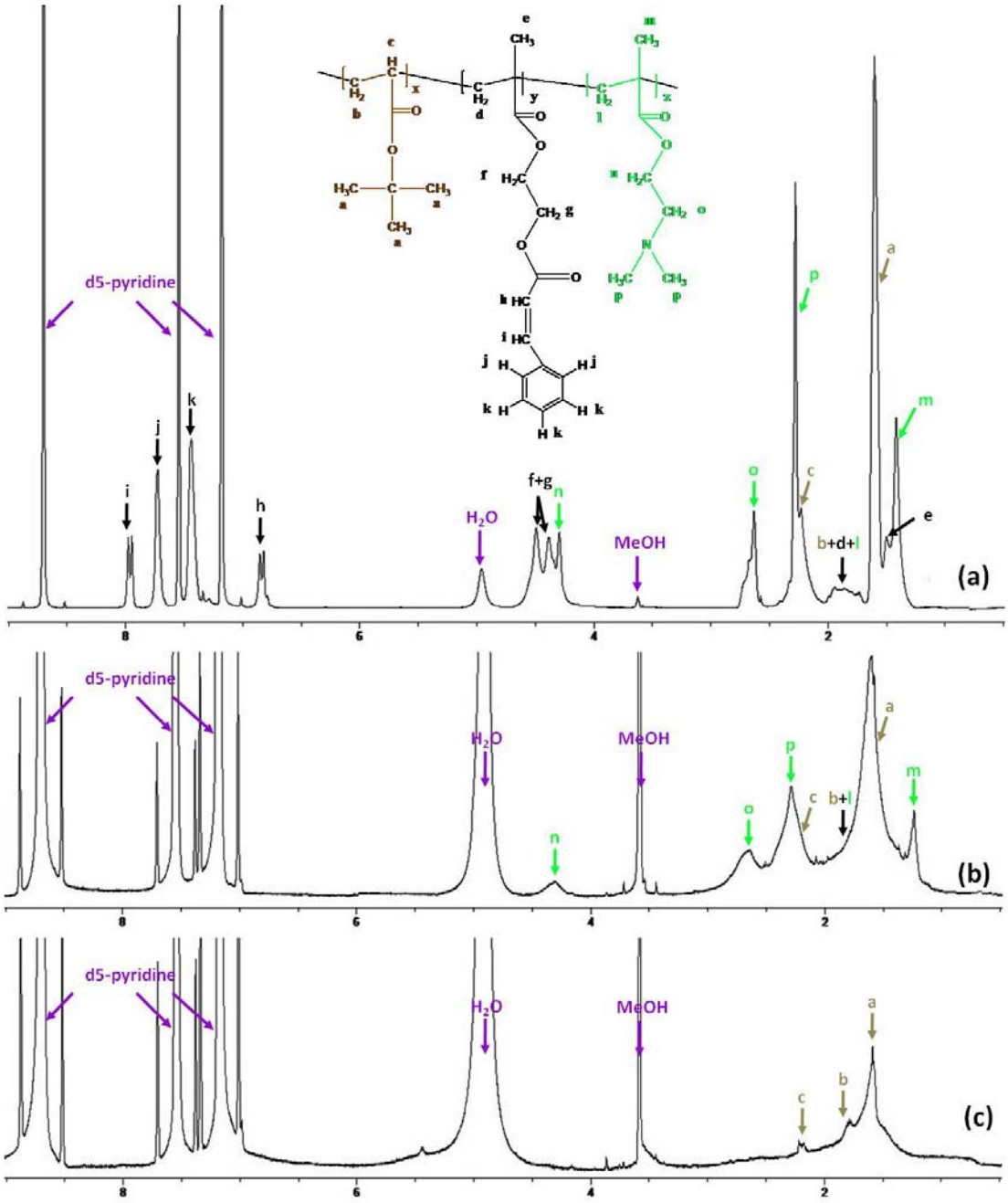


**Figure S2.** Comparison of the $^{1}H$ NMR spectra of (a) the PtBA-*b*-PCEMA-*b*-PDMAEMA triblock copolymer, (b) x-ANCs, and (c) core-shell-like composite nanofibers.

## References

1. X. Y. Li and G. J. Liu, *Langmuir*, 2009, **25**, 10811-10819.
2. G. Njikang, I. C. M. Kwan, G. Wu and G. J. Liu, *Polymer*, 2009, **50**, 5262-5267.