Electronic Supplementary Material (ESI) for Polymer Chemistry.

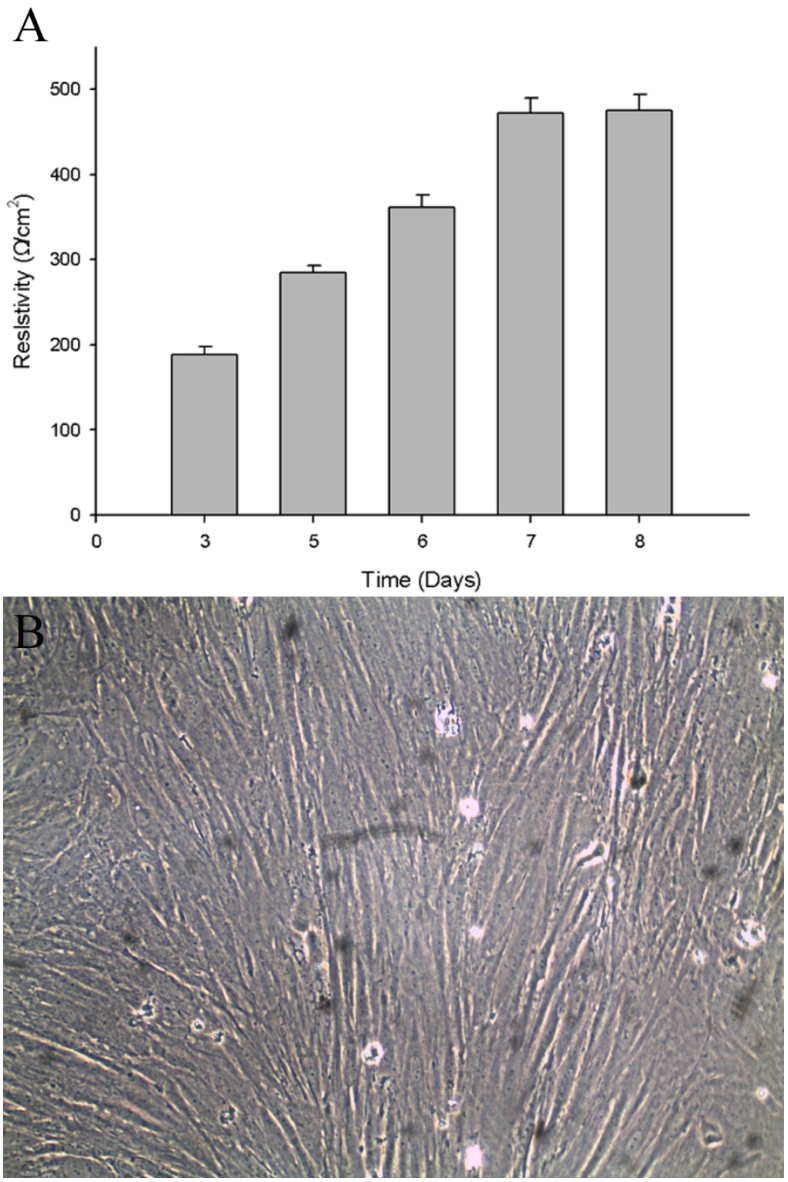

Figure S1. The resistance data of *in vitro* BBB model (A); The morphological characteristics of *in vitro* BBB model (B)

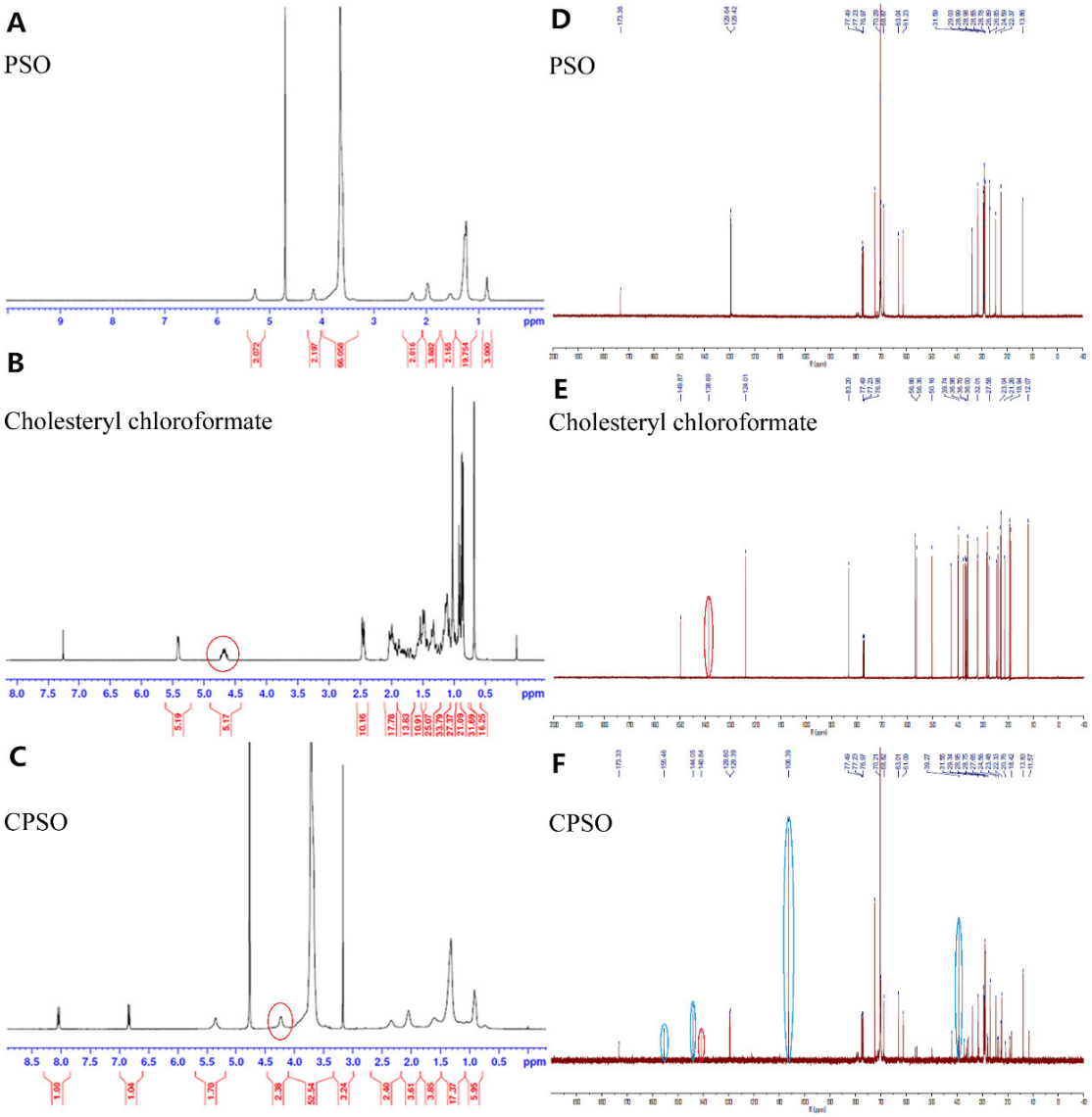

Figure S2. The H-NMR (A) and C-NMR (B) of PSO, Cholesteryl chloroformate and CPSO

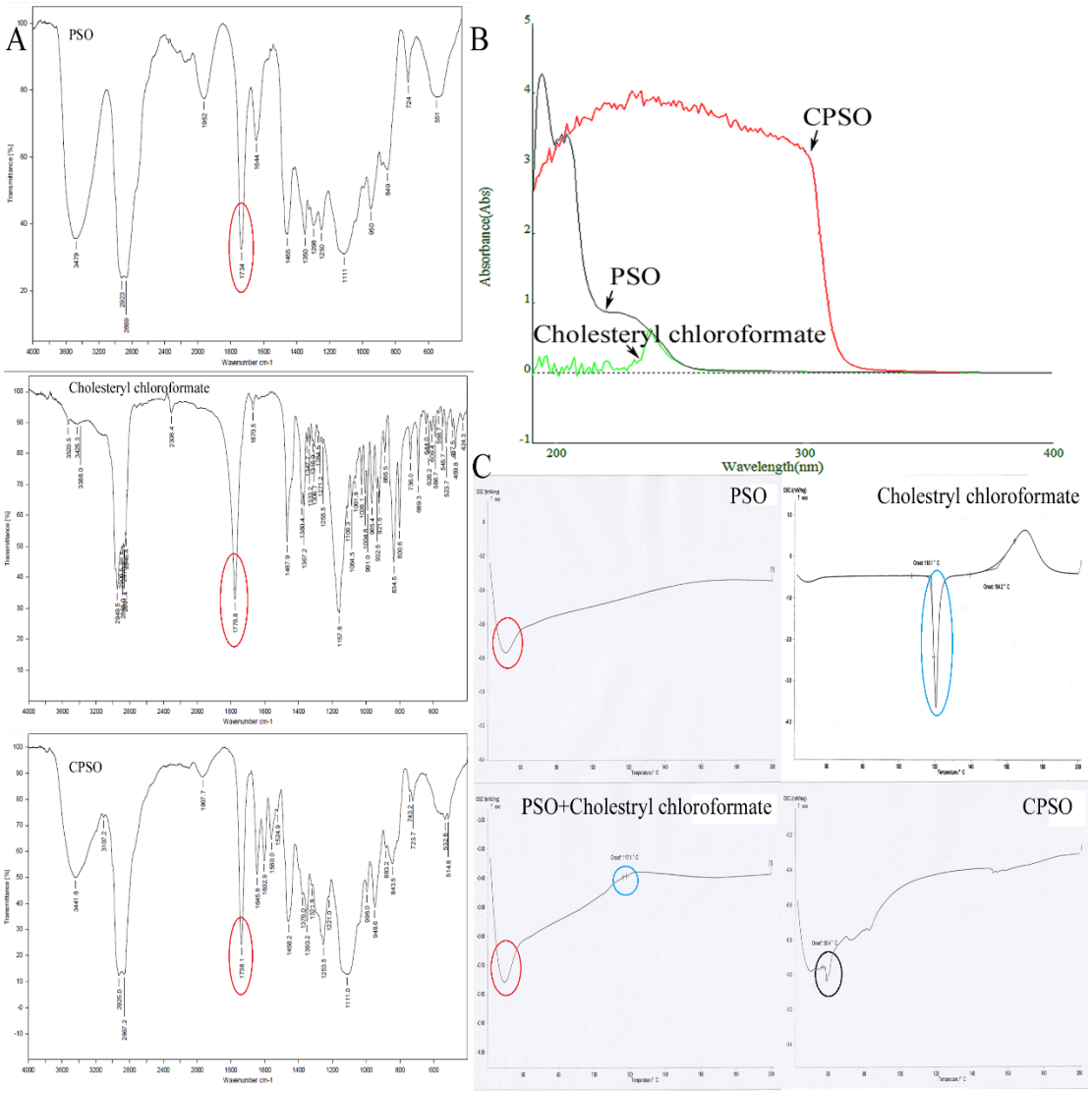

Figure S3. The IR of PSO, Cholesteryl chloroformate and CPSO (A); The UV/vis results of PSO, Cholesteryl chloroformate and CPSO (B); The DSC results of PSO, Cholesteryl chloroformate, physical mixture of polyoxyethylene sorbitol oleat and cholesterol and CPSO (C)

The structure of CPSO was confirmed by NMR, IR, UV/vis spectra and DSC as shown in Figure S1 C-F, respectively. As shown in H-NMR, the H (δ=4.7) nearby –OCOCl in cholesteryl chlorogormate shifted to δ=4.2 in the CPSO after conjugation. As shown in C-NMR of CPSO, the characteristic peaks at 39.27 ppm, 106.39 ppm, 144.05 ppm and 155.46 ppm belong to the carbon atoms in 4-dimethyl aminopyridine (DMAP). Notably, the carbon atom in carbonic ester, i.e., -OCO-, showed the characteristic peak at 140.84 ppm in Figure S2 F, while the corresponding peak in Figure S2 E is at 138.69 ppm. The small shift to a higher field reflected the incorporation of cholesterol to PSO. IR spectrum of PSO showed that the broad –OH stretching vibration peak appeared around 3479 cm^{-1}. While the C=O peak of oleic acid in PSO and chloroformate in cholesteryl chloroformate appeared at 1734 cm^{-1} and 1776.8 cm^{-1} respectively, It was noteworthy that, from IR spectrum of CPSO, a strong and new band at 1738.1 cm^{-1}, which is assigned to the carbonate carbonyl of CPSO. As shown in DSC, the characteristic peaks of PSO and cholesteryl chloroformate were both appeared in physical mixture sample, but there was a new peak at 58.4 ℃ appeared in CPSO sample. All these results indicated that the CPSO was successfully synthesized.