

Supporting Information

Sustained Release of a Synthetic Structurally-Tailored Glycopolymer Modulates Endothelial Cells for Enhanced Endothelialization of Materials

Shuaibing Jiang,^a Jingxian Wu,^a Yingjie Hang,^a Qi Liu,^a Dan Li,^{*a} Hong Chen^{*a} and
John L. Brash^{a,b}

^aState and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, 199 Ren'ai Road, Suzhou 215123, P. R. China

^bDepartment of Chemical Engineering and School of Biomedical Engineering, McMaster University, Hamilton, Ontario L8S4L7, Canada

Synthesis of 2-methacrylamido glucopyranose (MAG)

Successful synthesis of the saccharide monomer MAG was demonstrated by ¹H NMR (Figure S1) taken in D₂O at 400MHz.

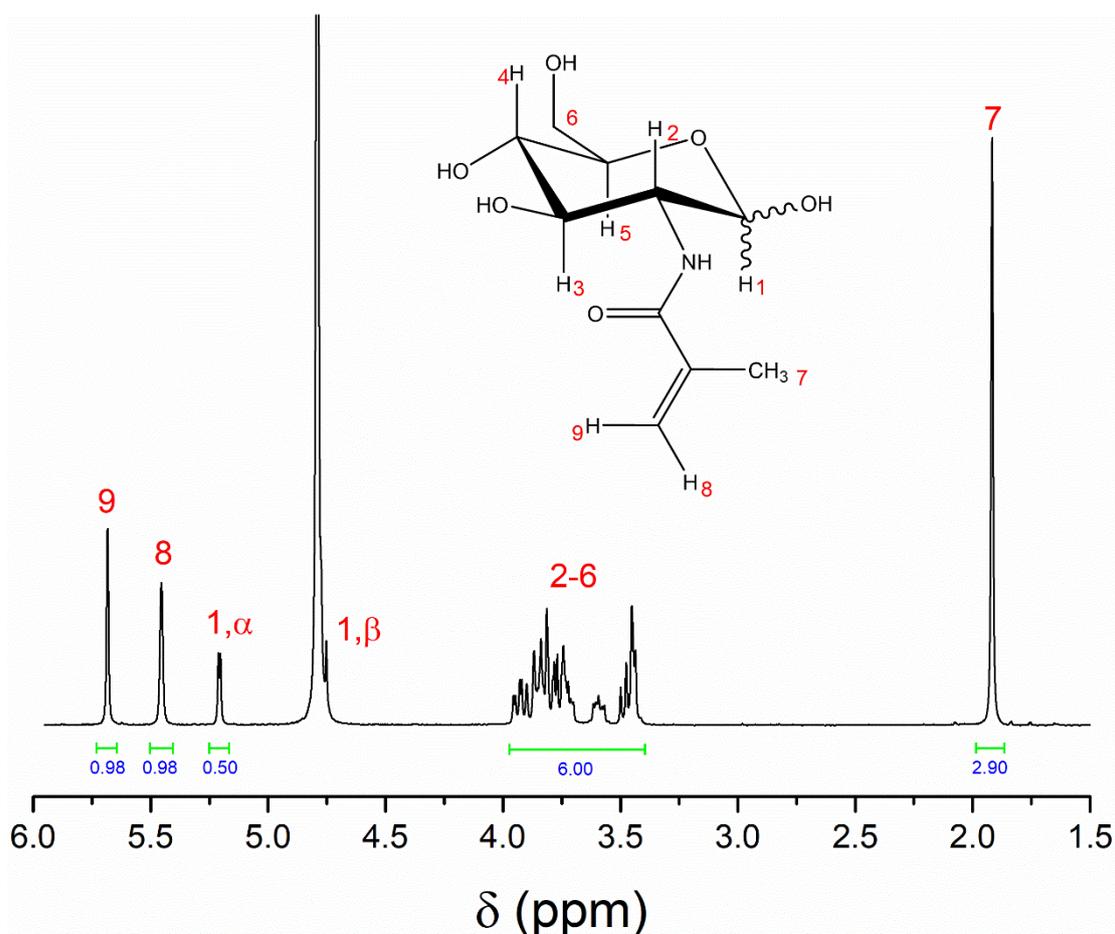


Figure S1. ¹H NMR spectrum of MAG in D₂O. H₁(α): 5.20-5.21 ppm (d, 0.50H), H₁(β): 4.75-4.77 ppm (d, 0.50H), H₂-H₆: 3.43-3.95 ppm (m, 6H), H₇: 1.92 ppm (s, 3H), H₈: 5.45 ppm (s, 1H), H₉: 5.68 ppm (s, 1H).

Synthesis of the GAG-mimicking glycopolymers (pS₁G₁)

Successful synthesis of pS₁G₁ was demonstrated by ¹H NMR (Figure S2) and FT-IR (Figure S3), respectively. The characteristic NMR peaks of SS (H₁-H₂) and MAG (H₃-H₇) can be clearly observed. In the FT-IR spectrum the peak at 3350 cm⁻¹ is attributed to the N-H/O-H bonds of MAG, the peaks at 1630 and 1532 cm⁻¹ are assigned, respectively, to the amide I band (stretch of C=O bond) and the amide II band (coupling of N-H bond bend and C-N bond stretch) of MAG. The peaks at 1170, 1123, 1034 and 1007 cm⁻¹ are assigned to the aryl SO stretch in SS.

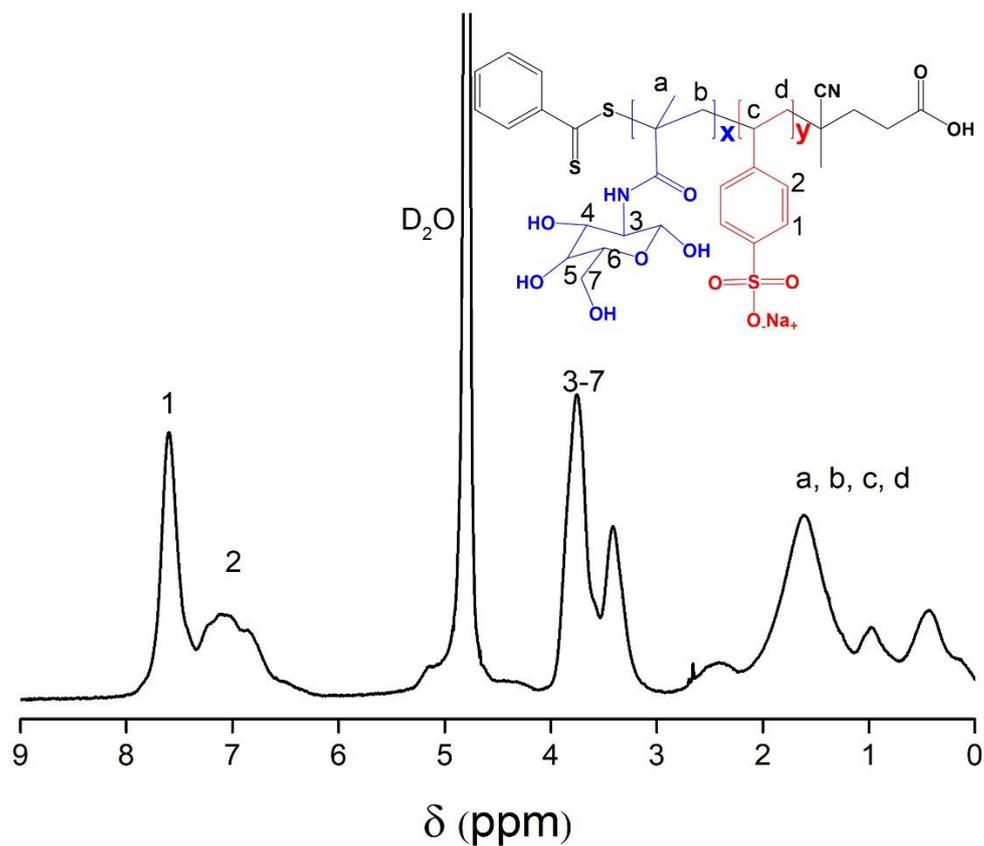


Figure S2. ^1H NMR spectrum of pSG in D_2O .

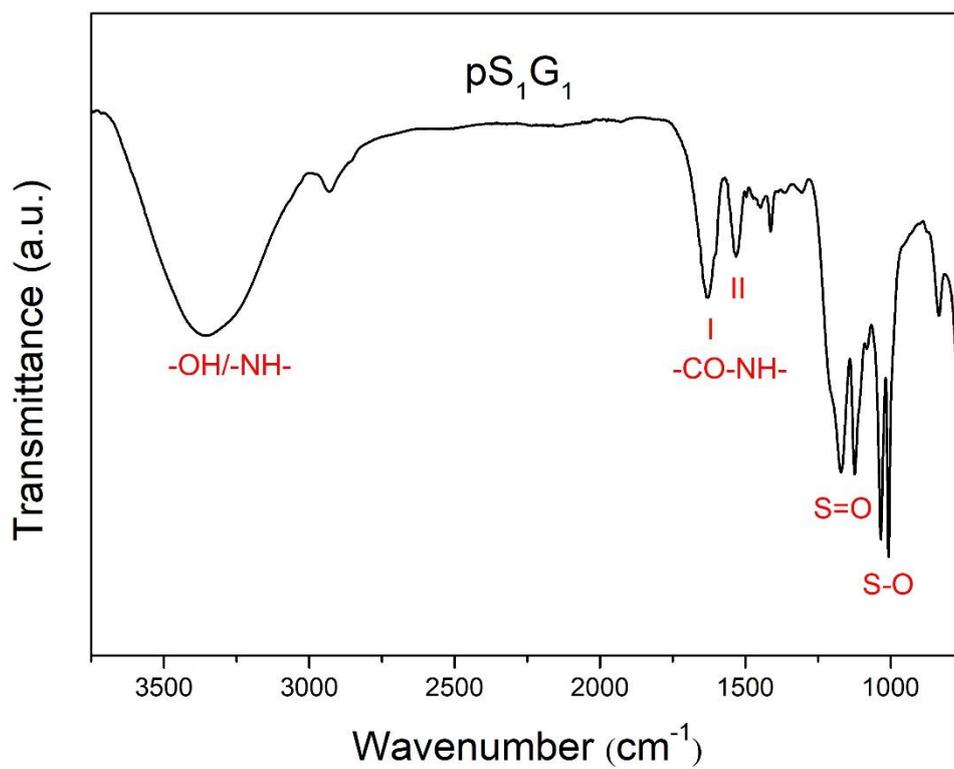


Figure S3. FT-IR spectrum of pS₁G₁.

Synthesis of fluorescently labeled GAG-mimicking glycopolymer (pSGF)

In order to visualize the glycopolymer in the core-shell nanofibers and to study its release profile, fluorescently labeled glycopolymer, pSGF, was synthesized and characterized. Briefly, SS (0.1547 g, 0.75 mmol), MAG (0.1853 g, 0.75 mmol), FluMA (Fluorescein O-methacrylate, 0.0123 g, 0.031 mmol), CTA (0.0043 g, 0.015 mmol), and AIBN (0.0013 g, 0.008 mmol) were dissolved in 4 mL of DMF/DIW mixed solvent (DMF:DIW = 1:1, v/v). The glycopolymer (pSGF) was synthesized using the same method as for the unlabeled polymer (see main text). Detailed information for pSGF is presented in [Figures S4-S8](#).

As shown in the ^1H NMR spectrum ([Figure S4](#)), the characteristic peaks of SS, FluMA ($\text{H}_1\text{-H}_2$) and MAG ($\text{H}_3\text{-H}_7$) are clearly visible, indicating successful copolymerization of the three monomers. In the FT-IR spectrum ([Figure S5](#)), the characteristic absorption peaks are assigned to SS and MAG, respectively, as described above. In addition, the C=O stretch of the ester group at 1742 cm^{-1} from pSGF is visible, indicating the successful copolymerization of FluMA with SS and MAG. The UV–visible spectrum ([Figure S6](#)) shows the maximum absorbance of pSGF at 440–470 nm. In addition, pSGF showed maximum fluorescence intensity with excitation at 456 nm and emission at 524 nm ([Figure S7](#)). As shown in [Figure S8](#), a GPC trace of pSGF was unimodal and the polydispersity index was low (1.21), suggesting that the copolymerization was well controlled. The number-average molecular weight (M_n) of pSGF was 7.6 kDa.

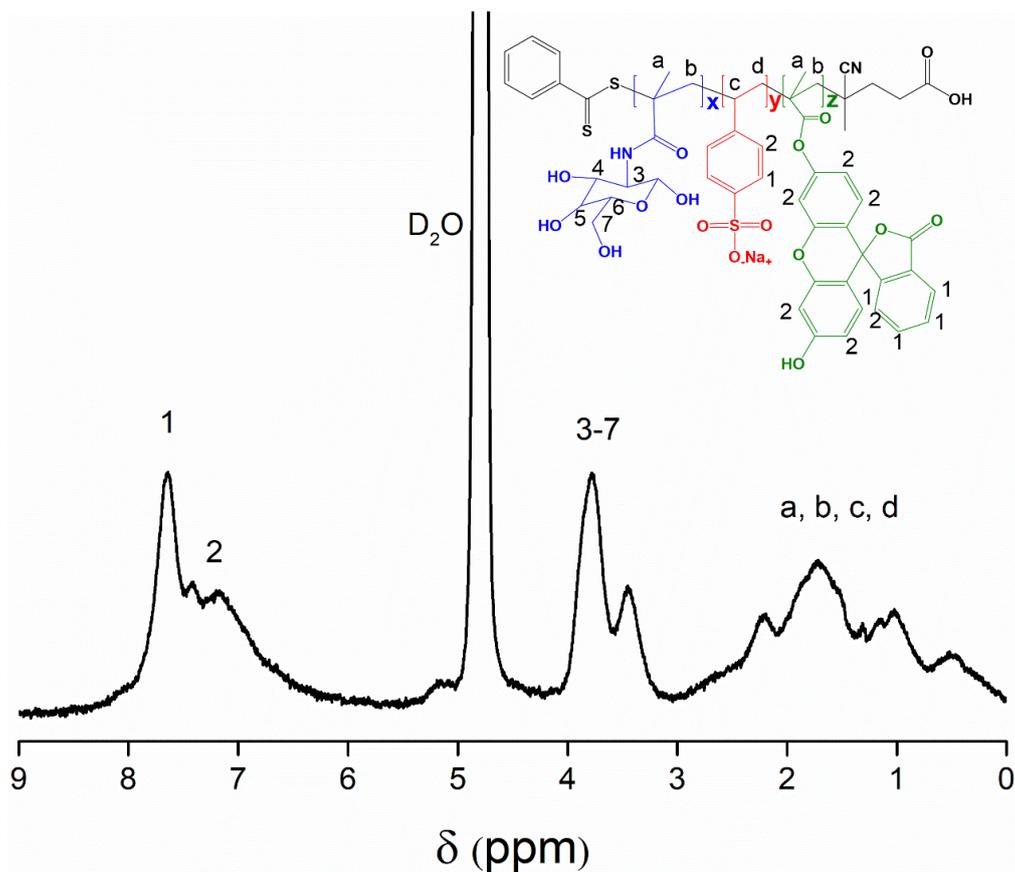


Figure S4. ^1H NMR spectrum of pSGF in D_2O .

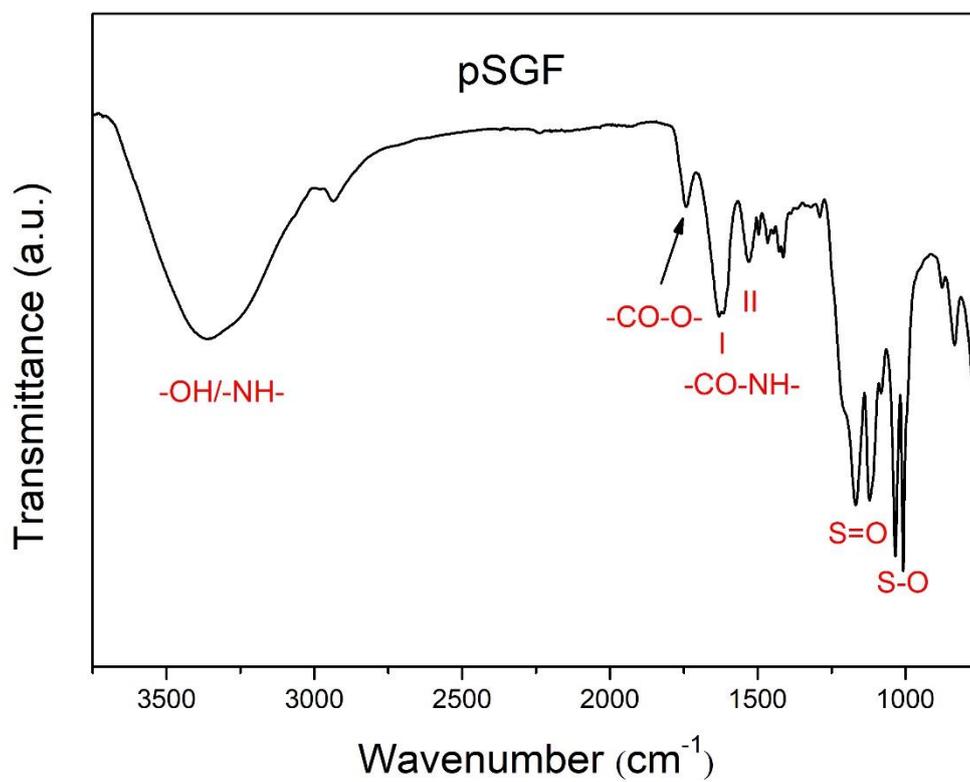


Figure S5. FT-IR spectrum of pSGF.

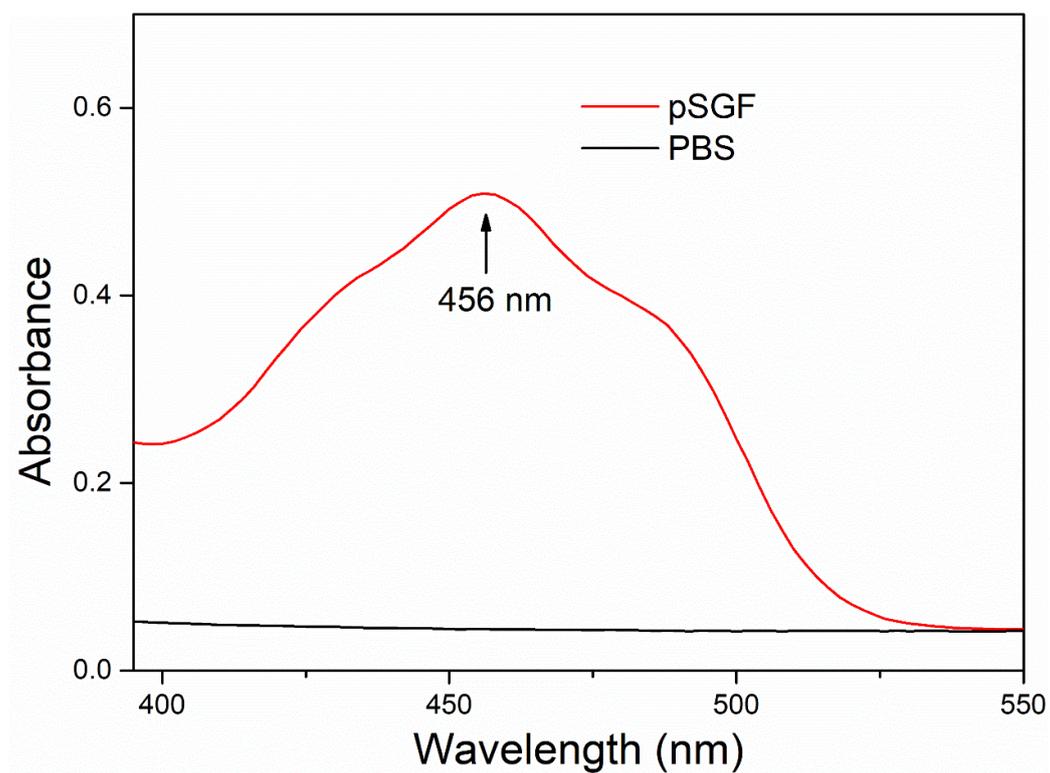


Figure S6. UV-Vis spectra of pSGF over wavelength range 400-550 nm. Maximum absorption pSGF at 448-478 nm.

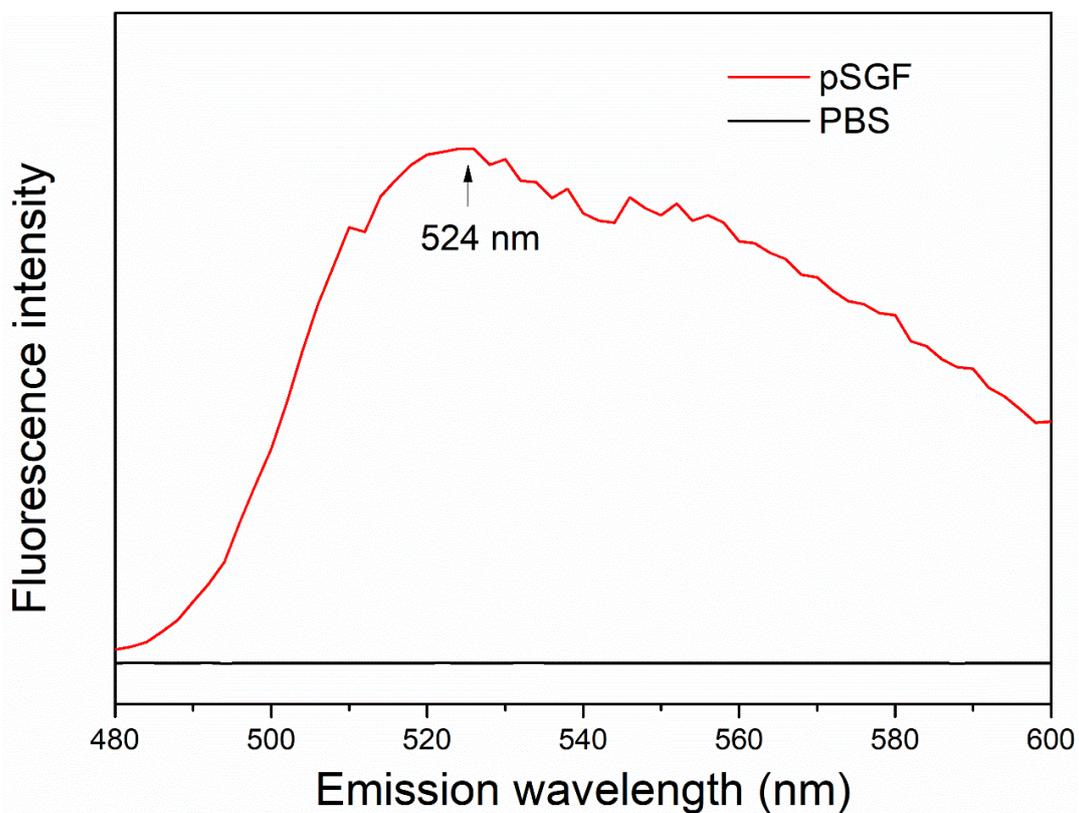


Figure S7. Fluorescence spectrum of pSGF excited at 456 nm, showing a high level of fluorescence intensity with maximum emission at 524 nm.

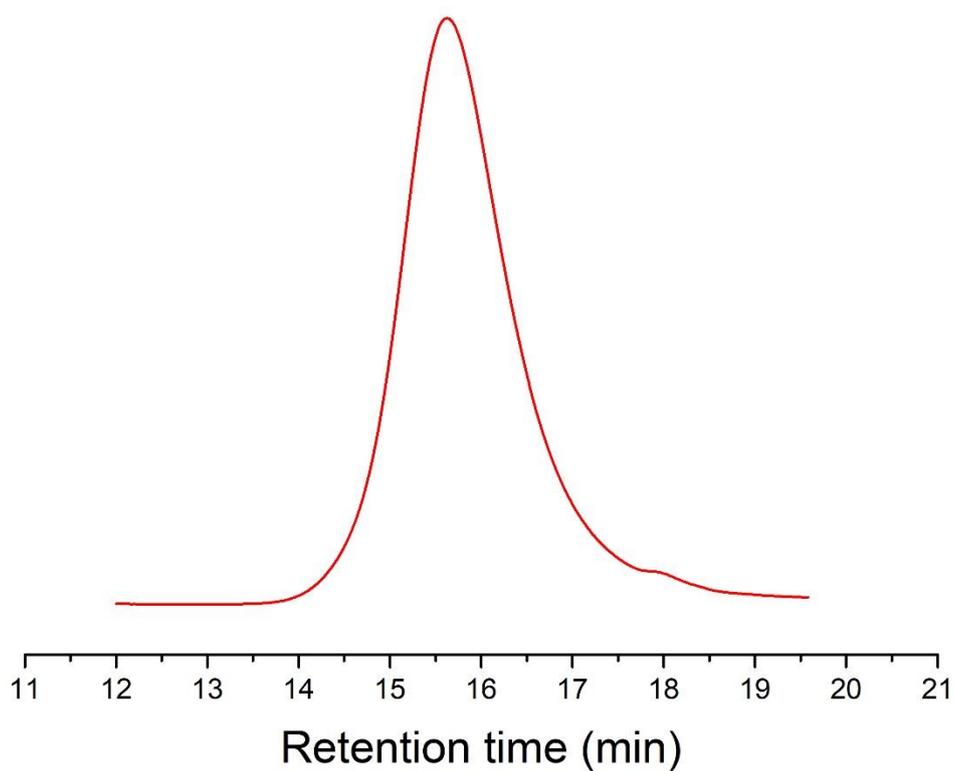


Figure S8. GPC trace of pSGF.

Table S1. Primers used in qRT-PCR.

Gene	Forward primer	Reverse primer	Product size (bp)
β-Actin	TTGCCGACAGGATGCA	AGGTGGACAGCGAG	129
	GAAGGA	GCCAGGAT	
PECAM-1	CAACGAGAAAATGTCA	GGAGCCTTCCGTTCT	259
	GA	AGAGT	
MCAM	AGAACCGGGTCCACAT	GTCGGGTAGAAAAC	193
	TCAG	AGGGAG	