Supporting Information

Super stretchable electroactive elastomer formation driven by aniline trimer self-assembly

Jing Chen, Baolin Guo, Thomas W. Eyster, Peter X Ma *

1. Materials

Aniline from J&K Scientific Ltd. was distilled twice under reduced pressure before use. L-lactide (LLA) was recrystallized in dry toluene and subsequently dried under reduced pressure (10^{-2} mbar) at room temperature for at least 48h before polymerization. Stannous octoate, $Sn(Oct)_2$ (Aldrich) was dried over molecular sieves and stored under a N_2 atmosphere before use. Ammonium persulfate, p-phenylenediamine, ethanol, n-propanal, polyethylene glycol (PEG), dimethylol propionic acid (DMPA), hexamethylene diisocyanate (HDI), tetrahydrofuran (THF), N-methyl-2-pyrrolidone (NMP), carbon black (CB), aniline, camphorsulfonic acid (CSA), dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), dicholoromethane (CH_2Cl_2) and hydrochloric acid (HCl) were purchased from Aldrich or J&K Scientific Ltd., and were used without any further treatment.

2. Characterization

FT-IR spectra of PLLA1500, AT, and copolymers were obtained from a Nicolet 6700 FT-IR spectrometer (Thermo Scientific Instrument). The spectra were taken as the average of 32 scans. The scans were ranged from 4000 to 650 cm^{-1} at a resolution of 4 cm^{-1}.

^1H NMR (400 MHz) spectra of PLLA1500, AT and prepolymers were recorded with

Bruker Ascend 400 MHz NMR instruments. DMSO-d_6 was used as the solvent for AT and all prepolymer samples and as an internal standard (δ 2.50 ppm) at room temperature. $CDCl_3$ was used as the solvent and internal standard (δ 7.26 ppm) for PLLA samples.

Gel permeation chromatography (GPC) measurements were carried out at 40 °C with a Waters 1525 pump, a column heater equipped with two Waters Styragel columns (HT2 and HT4) and a Waters 2414 refractive index detector. THF was chosen as an eluent at a flow rate of 1 mL/min. The standard curve of molecular weight was calibrated by linear polystyrene standards (Shodex SM-105).

The UV-visible spectra were obtained from a UV-vis spectrophotometer (PerkinElmer Lambda 35). Samples of AT and prepolymer were dissolved in DMSO and the wavelength was set from 250 to 1100 nm.

Cyclic voltammograms (CV) curves were recorded on a CHI 660D electrochemical workstation (CH Instruments) with a scanning rate of 10 mV/s. An ITO glass acted as a working electrode, and a platinum wire and an Ag/AgCl were used as counter and reference electrodes, respectively. The copolymer sample was coated on the working electrode ITO and immersed in a DMSO/ 1 mol/L HCl mixture; the solutions were then deoxygenated for 5 min before applying voltage. The data was recorded after 3 cycles.

The melting temperature (T_m) of the copolymers was measured by differential scanning calorimetry (DSC) using a Netzsch DSC under a nitrogen atmosphere (nitrogen flow rate of 50 mL/min). The samples were first heated to 200 °C and

equilibrated for 2 min to remove the thermal history. Data was recorded during the cooling from 200 to 20 °C and the heating scan from 20 to 200 °C at a heating rate of 10 °C/min. Values of melting points and crystallization enthalpy were obtained from the second heating scan.

Tensile tests were carried out by a MTS Criterion 43 equipped with a 50 N tension sensor. Copolymer films were cut into stripes (30 mm×6 mm×0.5 mm) and the crosshead speed was 15 mm/min. The tensile strength, breaking elongation and modulus data were taken as average of more than six samples.

Transmission electron microscopy (TEM) was performed on a HT-7700 (Hitachi) microscope at an acceleration voltage of 100 kV. A thin film of copolymer was deposited onto a copper grid from a 0.1% (wt/V) THF solution.

Dynamic light scattering (DLS) was used to detect the existence of AT aggregates in the copolymer's THF solution. The size of AT aggregates was collected by a Delsa Nano C analyzer (Beckman Coulter, Inc.).

Table S1. Molecular weight of the prepolymers

Sample name	M_n (k)	PDI
PEG1k-AT6	7.4	1.4
PEG2k-AT6	16.2	1.5
PEG4k-AT6	22.8	1.5
PEG6k-AT6	38.2	1.8
PEG2k-AT3	20.6	1.8
PEG2k-AT12	13.9	1.5
PEG2k-AT6-nD	23.7	1.9
PEG1k+4k-AT6	11.2	1.5

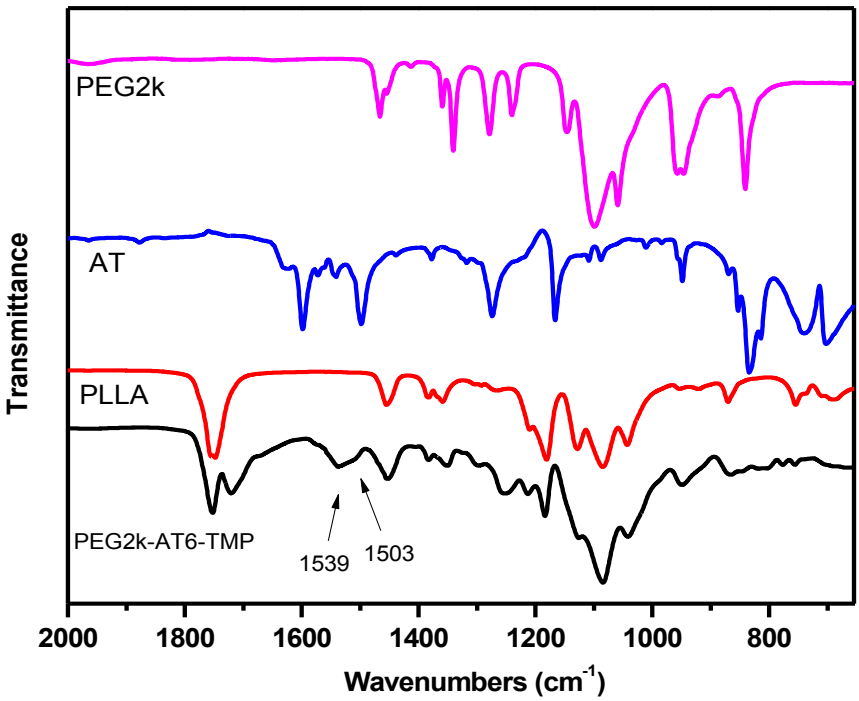


Figure S1. FT-IR spectra of monomers and macromeres employed in the synthesis of copolymer PEG2k-AT6-TMP.

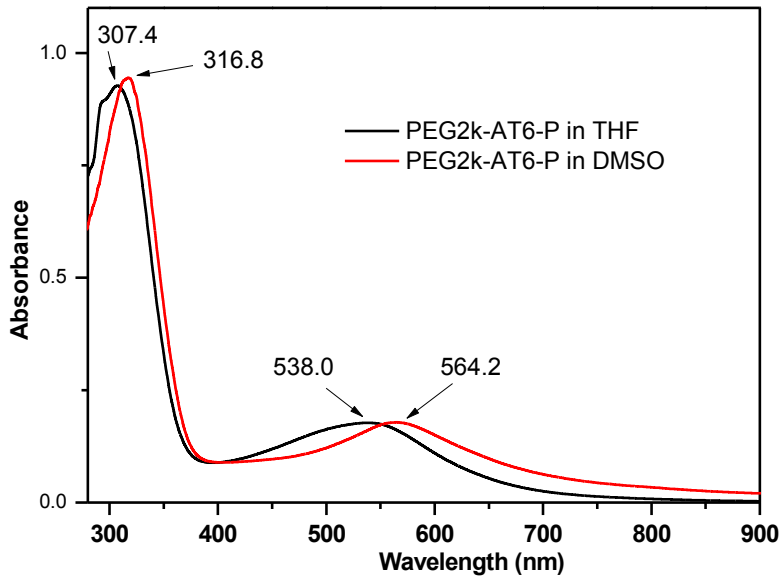


Figure S2. The UV-vis spectra of copolymer PEG2k-AT6-P in THF and DMSO

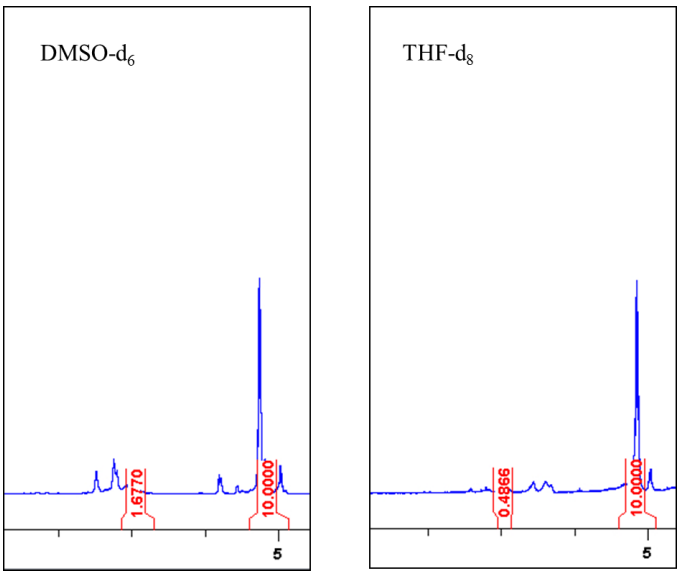


Figure S3. The ^{1}H NMR spectra of copolymer PEG2k-AT6-P in DMSO-d_6 and THF-d_8.

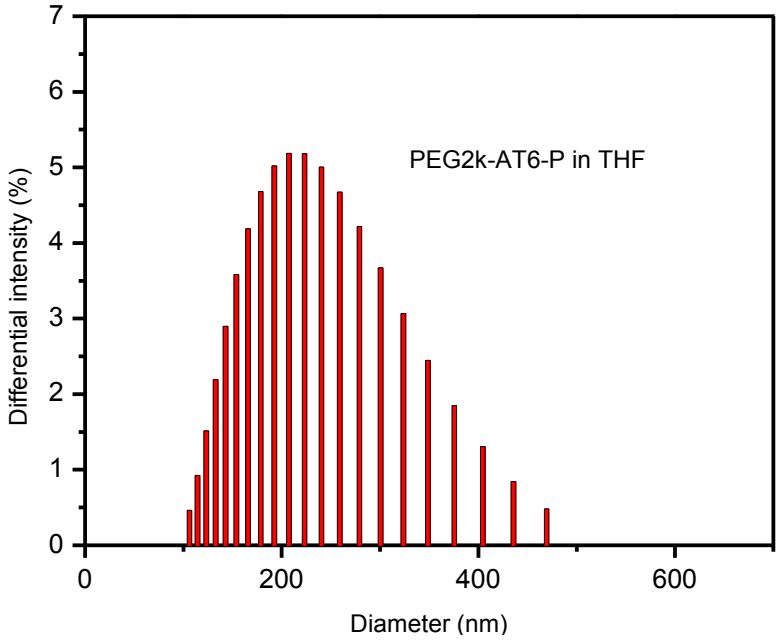


Figure S4. The size of AT aggregation of PEG2k-AT6-P in THF.

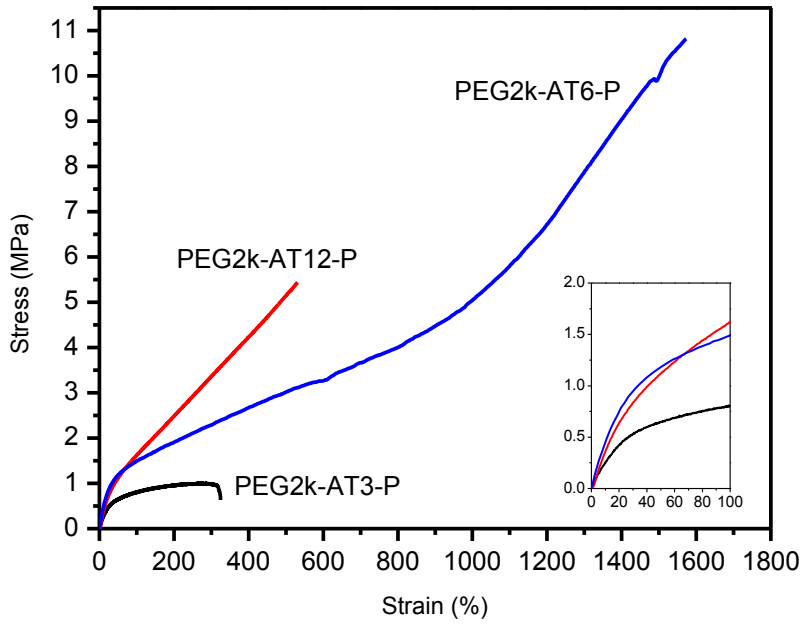
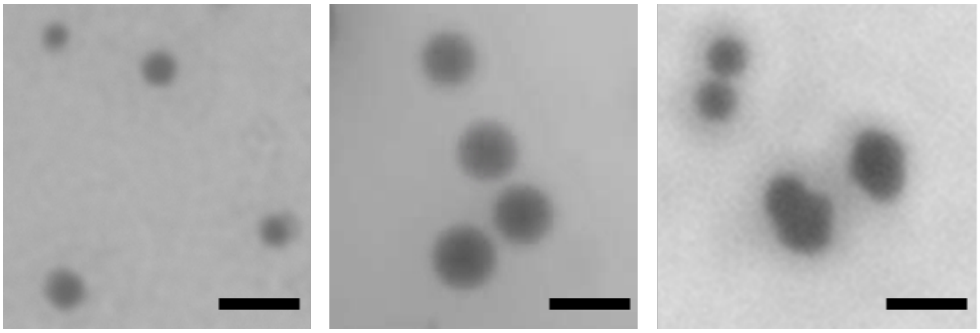


Figure S5. The strain-stress curves of PEG2k-AT3-P, PEG2k-AT6-P, and PEG2k-AT12-P samples.



a b c

Figure S6. The TEM pictures of samples with different AT contents: (a) PEG2k-AT3-P, (b) PEG2k-AT6-P, and (c) PEG2k-AT12-P. Scale bar: 200 nm.

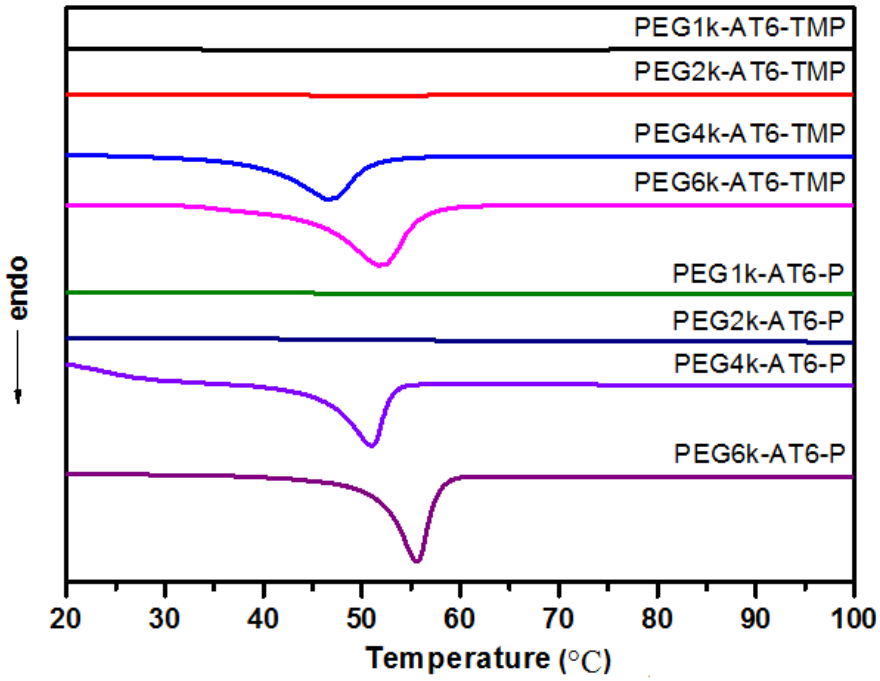


Figure S7. DSC curves of the copolymers and networks.

Table S2. The T_m and crystallinity of the copolymers

Samples	T_m (°C)	Crystallinity (%)
PEG1k-AT6-TMP	N/A	N/A
PEG2k-AT6-TMP	N/A	N/A
PEG4k-AT6-TMP	46.5	35.4
PEG6k-AT6-TMP	51.6	47.8
PEG1k-AT6-P	N/A	N/A
PEG2k-AT6-P	N/A	N/A
PEG4k-AT6-P	51.0	47.2
PEG6k-AT6-P	55.6	51.5

Table S3. Mechanical properties of copolymers

Samples	Strength (MPa)	Strain (%)	Young's Modulus (MPa)
PEG1k-AT6-TMP	1.3±0.1	333±5	6.0±0.8
PEG1k-AT6-P	3.4±0.15	530±82	3.0±0.57
PEG2k-AT6-TMP	10.1±0.8	1643±157	4.2±1.2
PEG2k-AT6-P	11.0±0.6	1573±63	3.8±0.2

PEG4k-AT6-TMP	6.5±0.5	597±68	29.2±1.6
PEG4k-AT6-P	9.0±0.52	437±26	199.0±5.17
PEG6k-AT6-TMP	8.2±1.1	242±4	189.9±8.2
PEG6k-AT6-P	12.8±2.04	374±10	323.0±14.17

Table S4. XPS result of the copolymers

	Binding energy (eV)	area ratio (%)	
		PEG2k-AT6-TMP	PEG2k-AT6-nD-TMP
C1s	289.4	8.19	7.73
	287.1	12.15	0
	286.0	29.16	12.55
	284.8	50.50	79.72
N1s	401.2	1.84	0
	400.2	48.94	32.02
	399.4	49.22	67.98

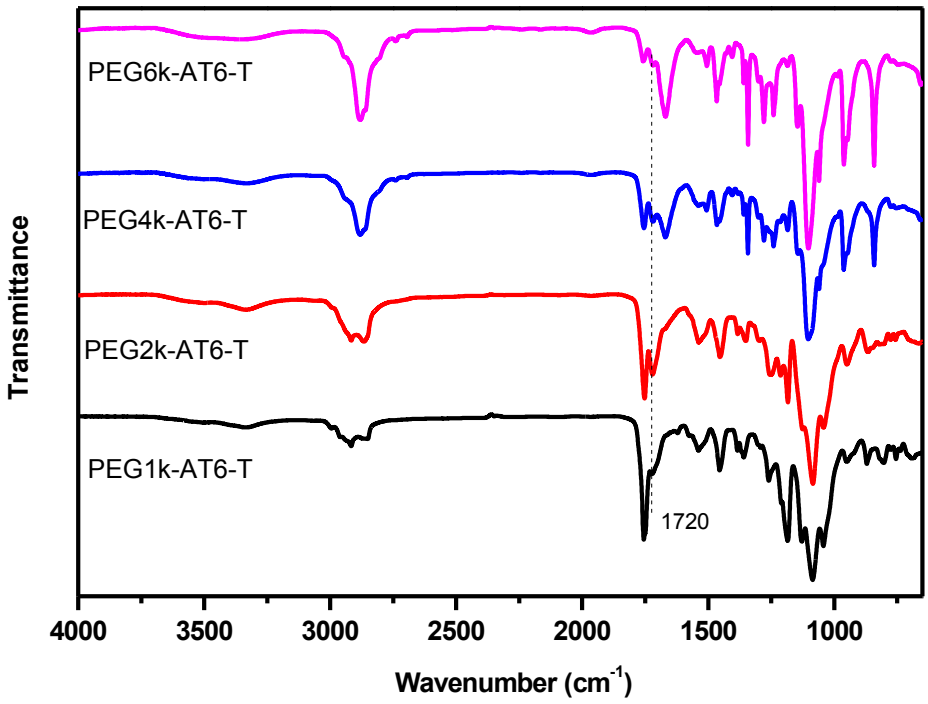


Figure S8. FT-IR spectra of networks with varied PEG segments.

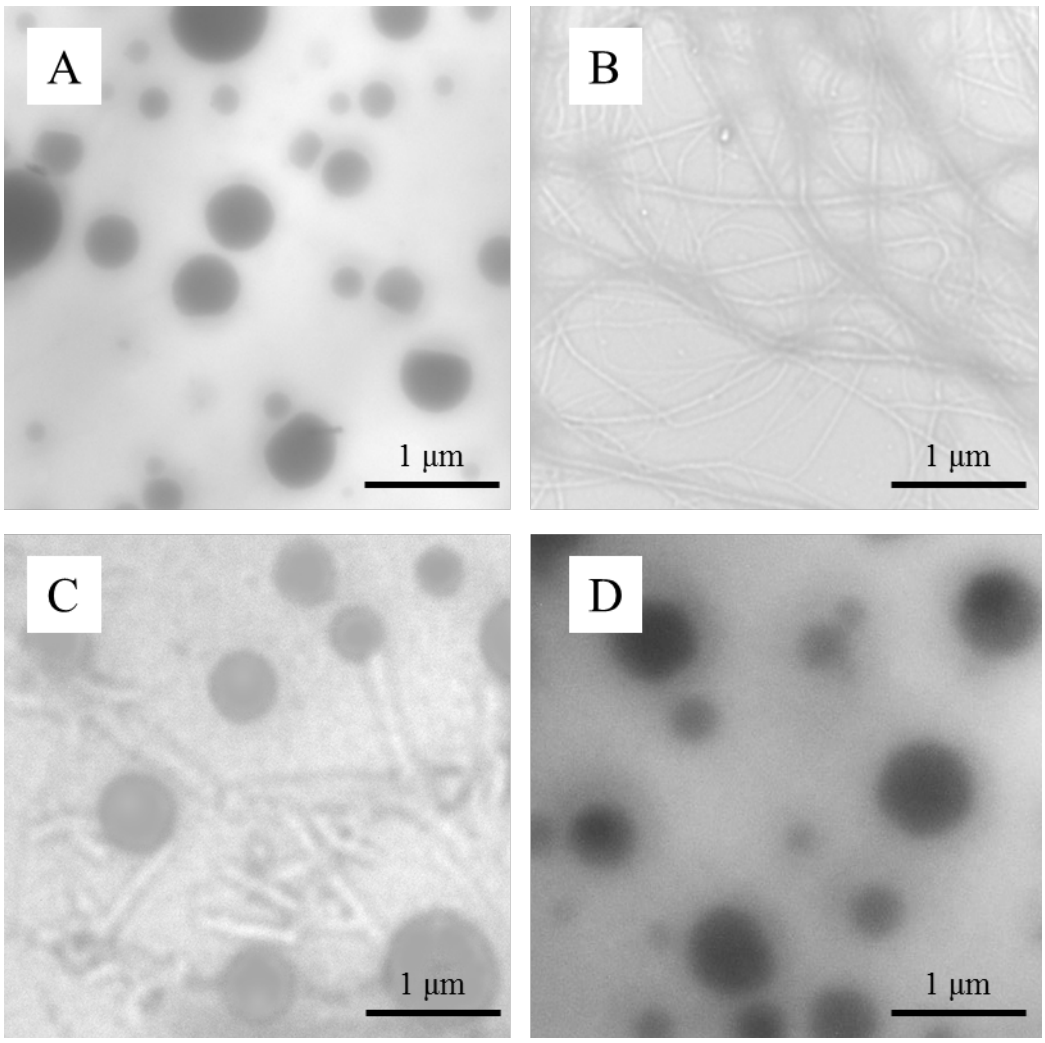


Figure S9. TEM pictures of: (A) PEG2k-AT6-P film, (B) 2% polyaniline nanofibers, (C) 2% polyaniline nanofibers/PEG2k-AT6-P blend film, and (D) 2% carbon black/PEG2k-AT6-P blend film.

Biocompatibility of copolymer films

To determine the cytotoxicity of PEG2k-AT3-P, PEG2k-AT6-P and PEG2k-AT12-P in comparison with PLLA, C2C12 cells were cultured with polymer extracts dissolved in media, and subsequently had their viability quantified using an alamaBlue assay. The result is shown in Figure S10. The fluorescence intensity (which represents cell viability in the presence of dissolved PEG2k-AT3-P, PEG2k-AT6-P and PEG2k-AT12-P) was higher at each concentration level than PLLA group ($p < 0.05$). The result indicates that PEG2k-AT3-TMP, PEG2k-AT6-P and PEG2k-AT12-P are

nontoxic in comparison to PLLA. All the data is expressed as mean ± standard deviation. Statistical comparison of the alamaBlue® assay of C2C12 cells proliferation was performed by the variance analysis of one-way ANOVA using the SPSS18.0 statistical package. A value of $p < 0.05$ was considered statistically significant.

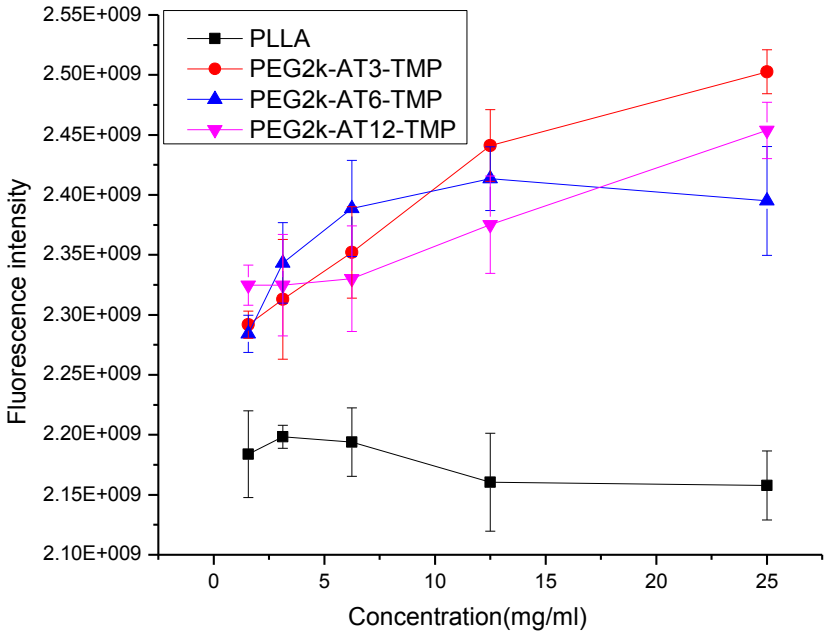


Figure S10. Cytotoxicity test of PEG2k-AT3-TMP, PEG2k-AT6-TMP and PEG2k-AT12-TMP in vitro.