Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supporting Documents

Synthesis of AMP-PEG-N_3 was carried out via carbodiimide coupling chemistry and was confirmed by ATR-FTIR spectroscopy as illustrated in Figure S-1.

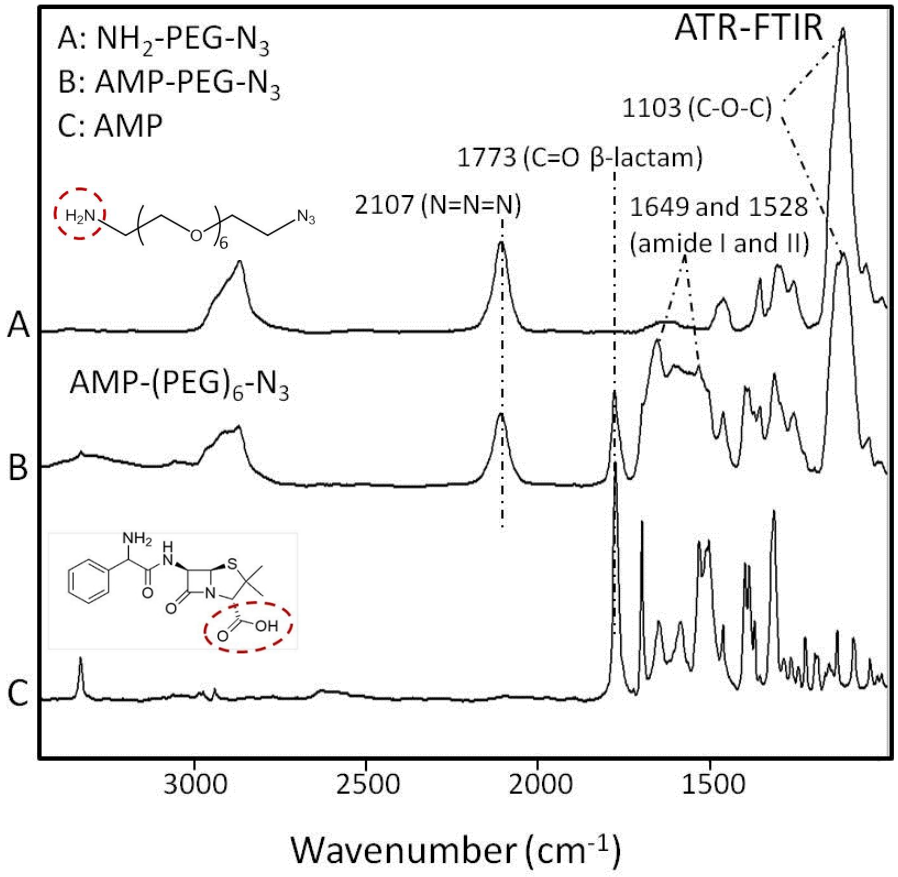

Figure S-1: ATR-FTIR spectra of A – NH_2-PEG-N_3 (Sigma-Aldrich); B – AMP-PEG-N_3; and C – AMP reference (reaction sites of A and C are circled).

Trace A illustrates an ATR-FTIR spectrum of NH_2-PEG-N_3 (Sigma-Aldrich), while Trace B shows the synthesized AMP-PEG-N_3 where the presence of the band at 2107 cm^{-1} is due to N=N=N stretching vibrations of the azide moiety, and the 1402 cm^{-1} band is due to C-O-C stretching vibrations of the PEG species. Trace C illustrates the FTIR spectrum of AMP with the band at 1773 cm^{-1} representing C=O stretching vibrations of the β-lactam moiety, which is also visible in the product (Trace B).[1] Additionally, Trace B contains bands at 1649 and 1528 cm^{-1} indicative of amide I and II linkages, respectfully, confirming the covalent reactions between NH_2-PEG-N_3 and AMP.

Experimental

All reagents were purchased from Sigma-Aldrich and used as received unless otherwise specified. Medical grade ultra-high molecular weight polyethylene (PE) and polypropylene (PP) were purchased from McMaster-Carr Supply Co. (Atlanta, GA), cut into 1 x 1 cm squares, washed in isopropanol, and dried at room temperature in a desiccator before use. To obtain -COOH terminated PE and PP surfaces, microwave plasma reactions were conducted in the presence of maleic anhydride (MA) under open reactor conditions, as described elsewhere.[2] In the next step, several approaches were used to determine the optimal method of alkyne functionalization. Initially, PP with –COOH surface functionalities were placed with 0.1 mmol diglycidyl ether polyethylene glycol (PEG) (M_n = 526) and 1 – 2 drops Et_3N in 10 ml DMF and stirred at 50 °C for 24 h. Samples were rinsed in DMF followed by immersion into 5 ml anhydrous dimethylfurane (DMF) with 1 g propargylamine. 1 drop of Et_3N was added to the solution and stirred under N_2 atmosphere for 120 h. The surfaces were rinsed in DMF followed by washing with DI water and stored in a desiccator. Additional PP surfaces exhibiting –COOH groups were reacted with propargylamine via carbodiimde coupling chemistry by dissolving 1.3 mM dicyclohexyl-carbodiimide (DCC) coupling agent and 0.25 mM 4-(dimethylamino)-pyridine (DMAP) catalyst in 20 mL methylene chloride and stirred for 16 h. The samples were then removed and placed into 5 ml anhydrous 2-propanol (IPA) with 1 g propargylamine. 1 drop of Et_3N was added to the solution and stirred under N_2 atmosphere for 120 h. The surfaces were rinsed in IPA followed by washing with DI water and stored in a desiccator. Similarly, PE and PP surfaces containing –COOH groups were placed in neat oxalyl chloride for 2 hrs to create -COCl groups and rinsed in chloroform before immediate immersion into 5 ml anhydrous IPA with 1 g propargylamine. 1 drop of Et_3N was added to the solution and stirred under N_2 atmosphere for 120 h. The surfaces were rinsed in IPA followed by washing with DI water and stored in a desiccator.

Ampicillin Azide Synthesis

AMP-PEG-N_3 (Sigma-Aldrich) was prepared via carbodiimde coupling chemistry by dissolving 1.3 mM 1-ethyl-3-(dimethylaminopropyl) carbodiimide (EDAC) coupling agent

and 0.25 mM *N*-hydroxysuccinimide (NHS) catalyst, as well as 0.15 g of ampicillin (AMP) in 1.5 mL DI water, then mixing the solution with 0.10 g O-(2-aminoethyl)-O'-(2-azidoethyl)pentaethylene glycol (NH_2-PEG_6-N_3). The solution was stirred at room temperature for 48 h, at which time an aliquot was taken for ATR FT-IR analysis to confirm the formation of AMP-PEG-N_3.

Click Reactions of AMP on PE/PP Surfaces

Aqueous click reactions were carried out using methods outlined elsewhere[330] between alkyne functionalized PP and PE surfaces and AMP-PEG-N_3. PE and PP surfaces previously reacted with propargylamine were added to 0.5 mmol AMP-PEG-N_3 and 0.05 mmol sodium ascorbate in 2 mL of DI water. 0.01 mmol of $CuSO_4$ was added to the mixture and stirred at room temperature for 18 h. The surfaces were then washed twice in DI water and stored in a desiccator prior to use. The drop plate method adopted from the literature was utilized for counting antimicrobial activity against *S. aureus.*[4]

Surface Characterization

Attenuated total reflectance Fourier transform infrared (ATR FT-IR) spectra were collected using a Bio-Rad FTS-6000 FT-IR single-beam spectrometer set at a 4 cm^{-1} resolution equipped with DTGS detector and a 45º face angle Ge crystal. Each spectrum represents 200 co-added scans ratioed against a reference spectrum obtained by recording 200 co-added scans of an empty ATR cell. All spectra were corrected spectral distortions using Q-ATR software.[1]

Raman spectra were obtained using a Renishaw Raman microscope-spectrometer equipped with a computer controlled three-axis encoded motorized stage, a RenCam CCD detector, and a Leica microscope (DMLM series). The 785 nm diode laser provided an excitation source with a maximum power output of 300 mW. Raman spectra were for each sample at 30 mW laser power at an acquisition time of 10 sec.

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2. Aumsuwan, N.; Heinhorst, S.; Urban, M. W., Antibacterial surfaces on expanded polytetrafluoroethylene; penicillin attachment. *Biomacromolecules* **2007,** 8, 713.
3. Ossipov, D. A.; Hilborn, J., Poly(vinyl alcohol)-based hydrogels formed by "click chemistry". *Macromolecules* **2006,** 39, 1709.
4. Herigstad, B., M. Hamilton,and J. Heersink, "How to Optimize the Drop Plate Method for Enumerating Bacteria," *J. Microbiol. Methods*, 44(2): 1 (2001).