

## SUPPORTING INFORMATION

### **Azide-substituted polylactide: A Biodegradable Substrate for Antimicrobial Materials via Click Chemistry Attachment of Quaternary Ammonium Groups**

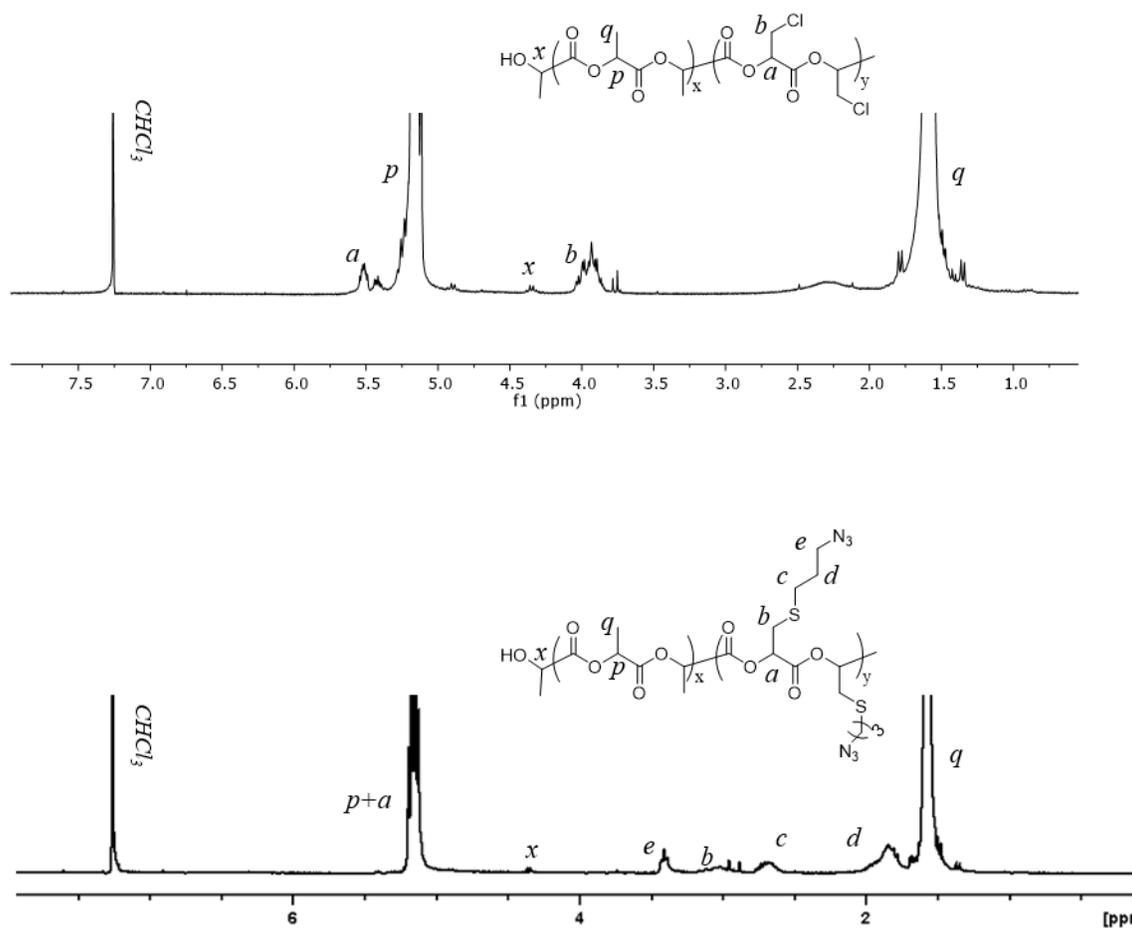
Pranav P. Kalelkar,<sup>a</sup> Zhishuai Geng,<sup>a</sup> M.G. Finn<sup>a,b</sup> and David M. Collard<sup>a\*</sup>

<sup>a</sup>School of Chemistry and Biochemistry, <sup>b</sup>School of Biological Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA, 30332-0400.

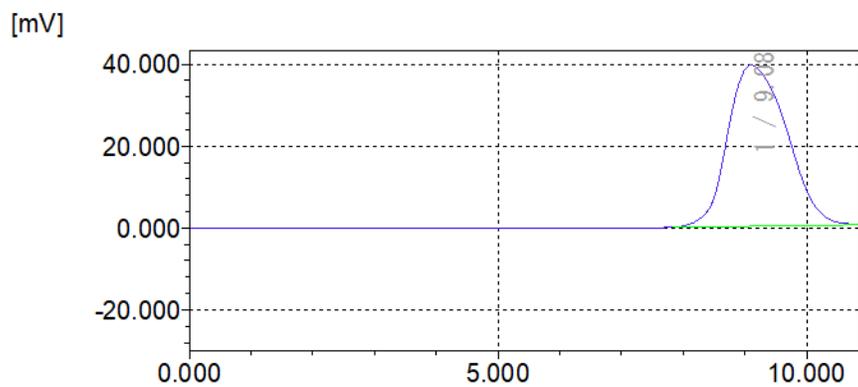
---

\* author to whom correspondence should be addressed

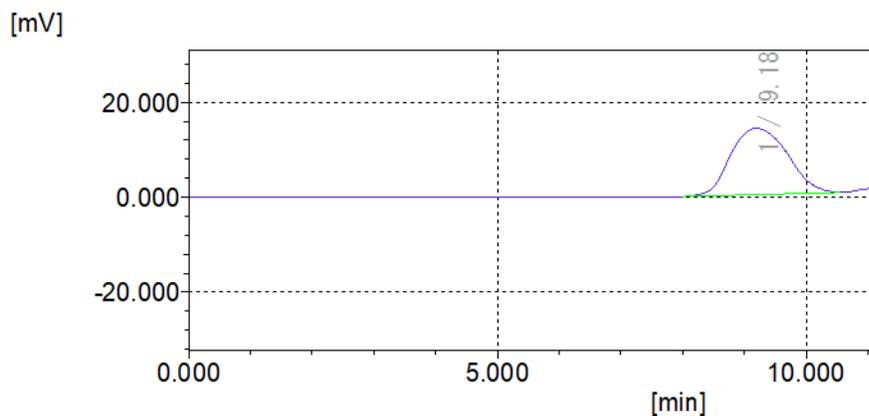
## Supporting Figures



**Figure S-1.** <sup>1</sup>H NMR spectra (300 MHz, CDCl<sub>3</sub>). Top, chloro-PL; Bottom, azido-PL obtained from one-pot dehydrochlorination and thiol addition



	[min]	[mV]	[mol]		[min]
Peak start	7.993	0.110	51,677	Mn	6,405
Peak top	9.180	14.492	8,671	Mw	9,056
Peak end	10.563	0.999	1,082	Mz	12,261
				Mz+1	15,779
				Mv	9,056
Height [mV]			13.972	Mp	8,650
Area [mV*sec]			894.236	Mz/Mw	1.354
Area% [%]			100.000	Mw/Mn	1.414
[eta]			9055.80933	Mz+1/Mw	1.742

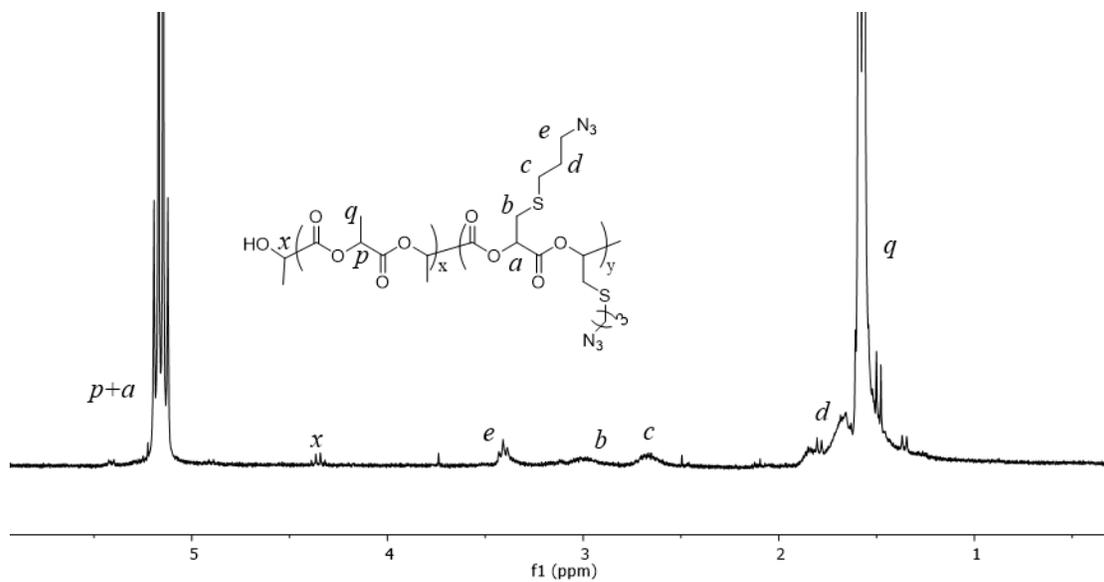


Result of molecular weight calculation (RI)

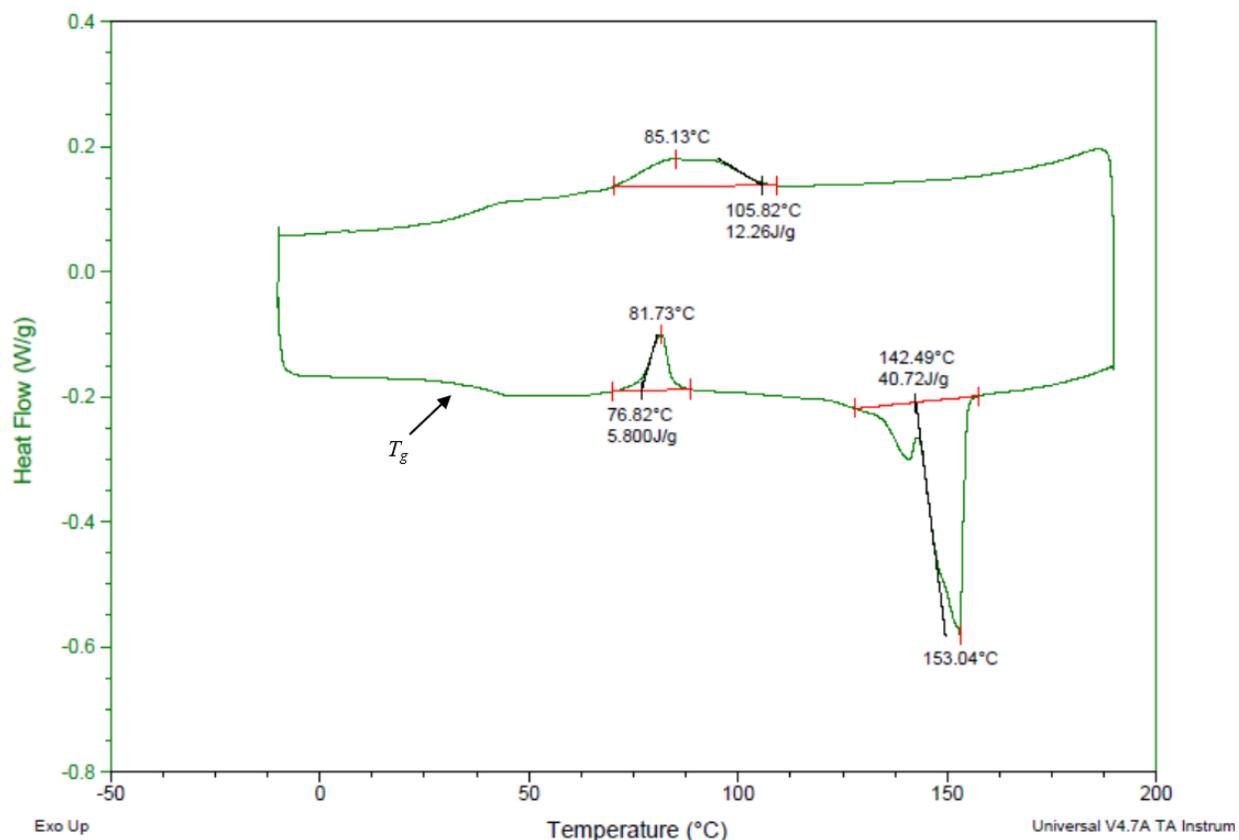
Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	7.993	0.110	51,677	Mn	6,405
Peak top	9.180	14.492	8,671	Mw	9,056
Peak end	10.563	0.999	1,082	Mz	12,261
				Mz+1	15,779
				Mv	9,056
Height [mV]			13.972	Mp	8,650
Area [mV*sec]			894.236	Mz/Mw	1.354
Area% [%]			100.000	Mw/Mn	1.414
[eta]			9055.80933	Mz+1/Mw	1.742

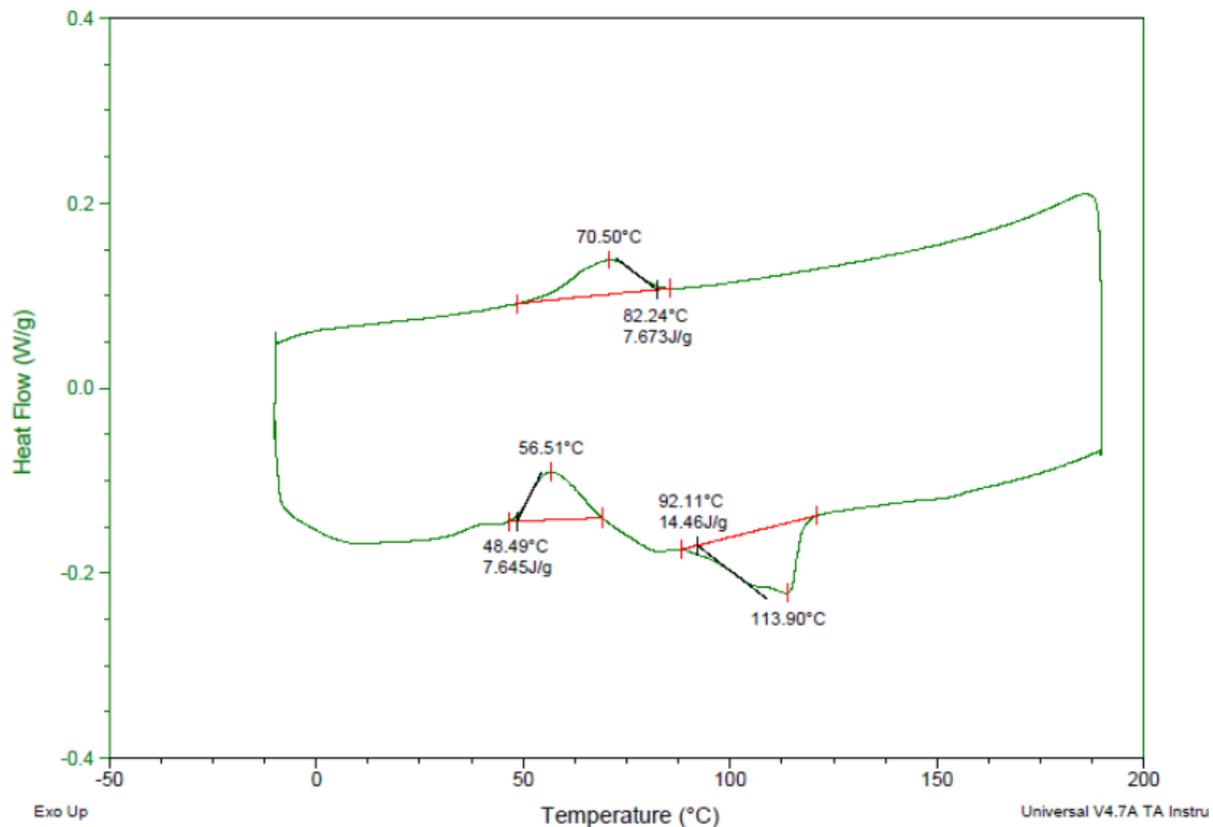
**Figure S-2.** Gel permeation chromatography (GPC) in THF, calibrated with polystyrene standards. Top, azido-PL; Bottom, 4-methoxybenzoate-substituted PL.



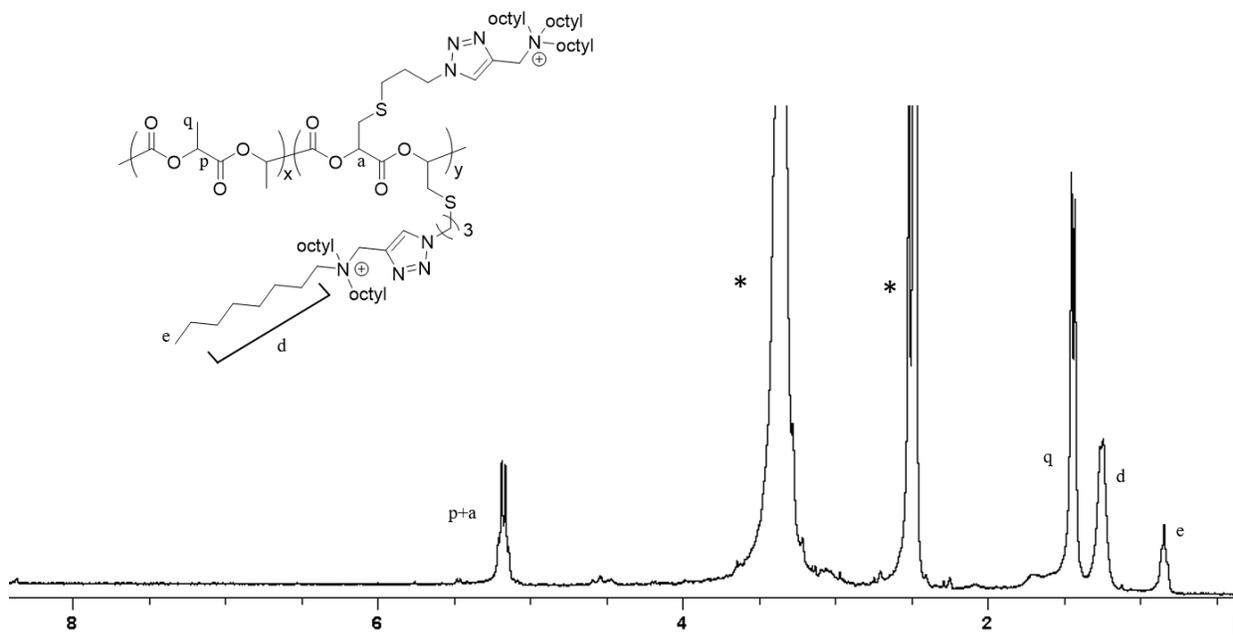
**Figure S-3.** <sup>1</sup>H NMR spectra (300 MHz, CDCl<sub>3</sub>). azido-PL obtained upon treatment with triethyl amine



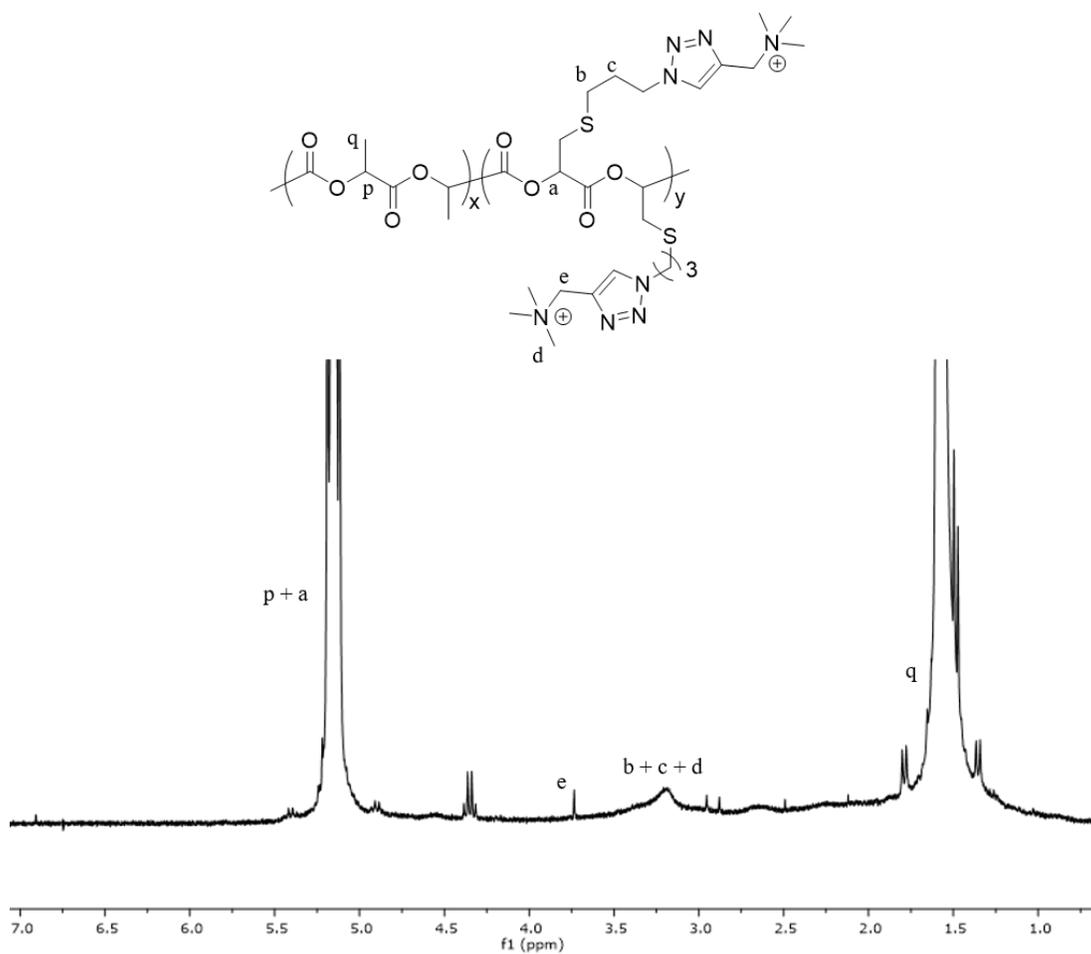
**Figure S-4.** Differential Scanning Calorimetry (DSC) (5 °C/min, from -10 °C to 180 °C) of azido-PL.



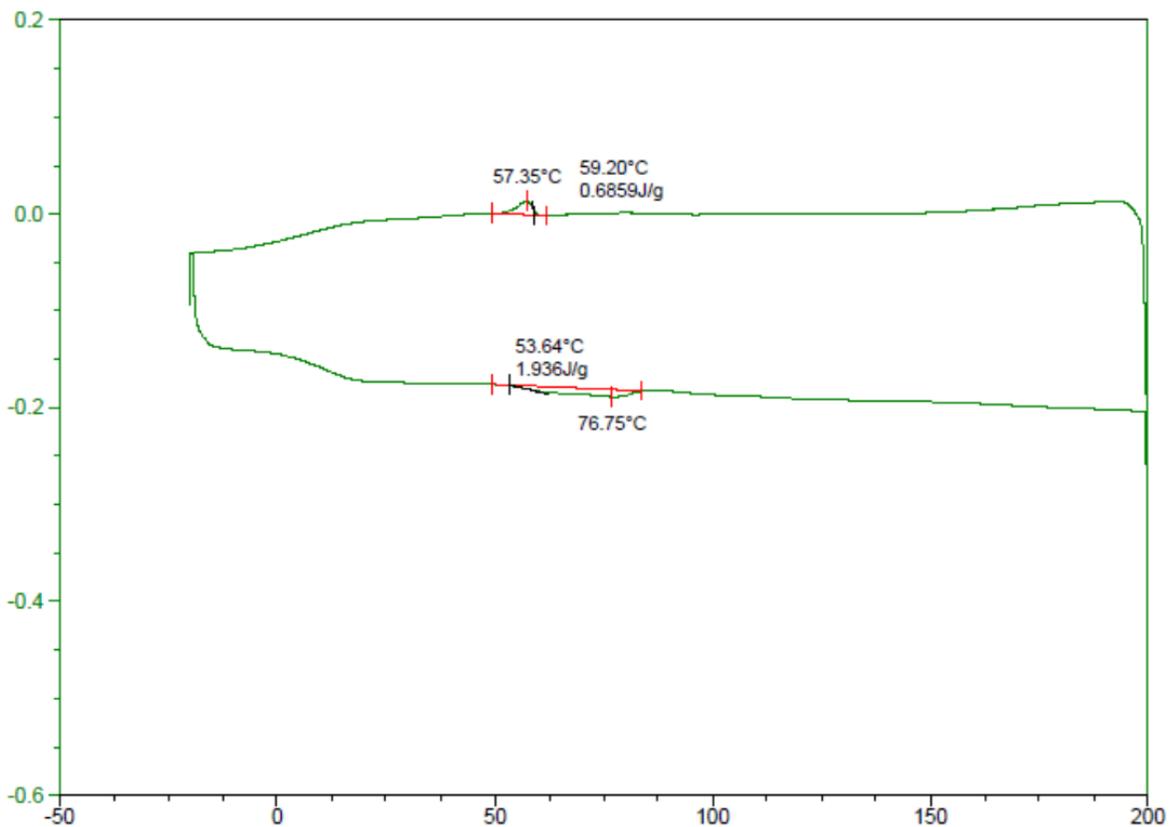
**Figure S-5.** Differential Scanning Calorimetry (DSC) (5 °C/min, from -10 °C to 180 °C) of 4-methoxybenzoate-substituted PL.



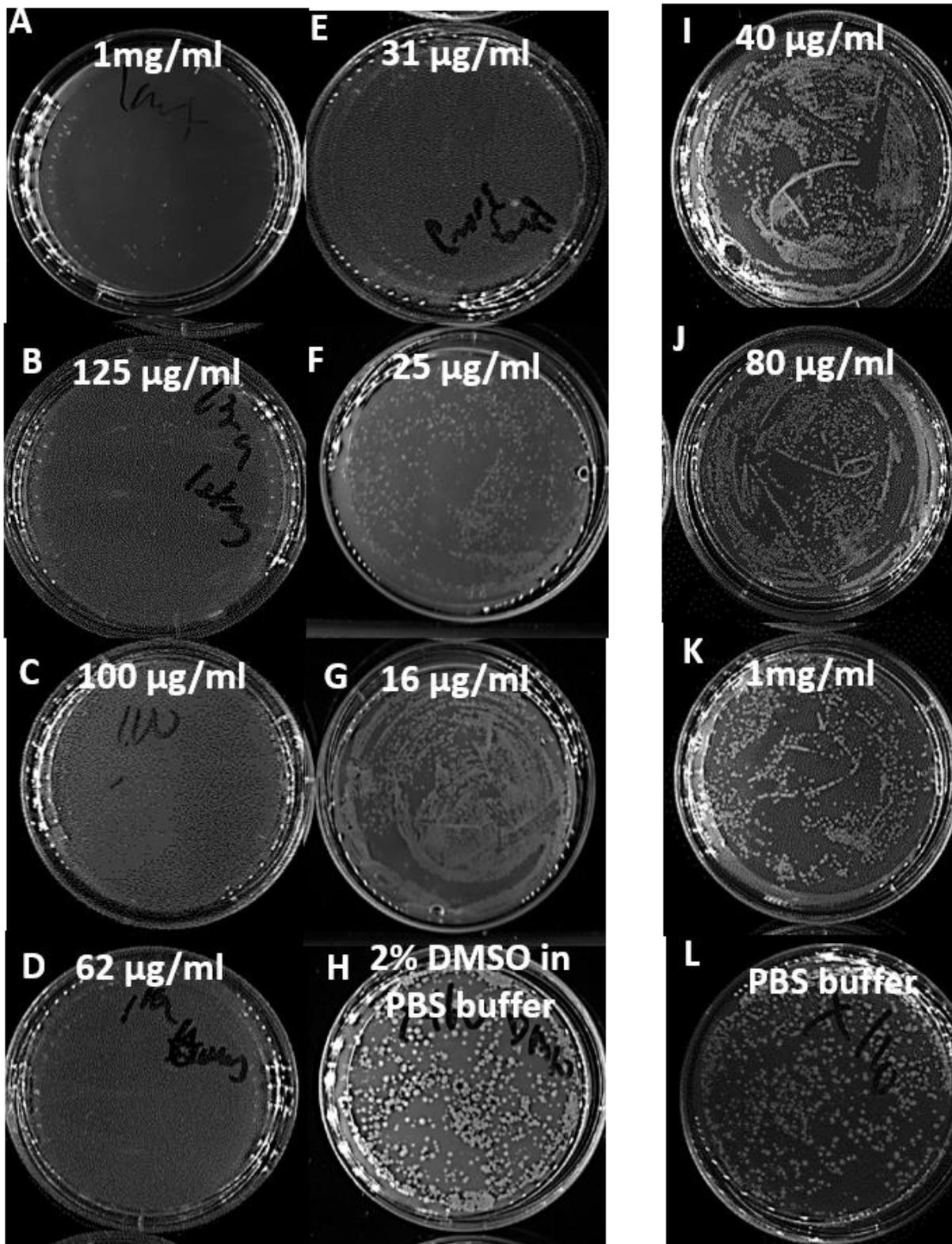
**Figure S-6.** <sup>1</sup>H NMR spectrum (300 MHz, DMSO-d<sub>6</sub>) of Trioctylammonium-substituted PL.  
 \*residual solvents-H<sub>2</sub>O, DMSO



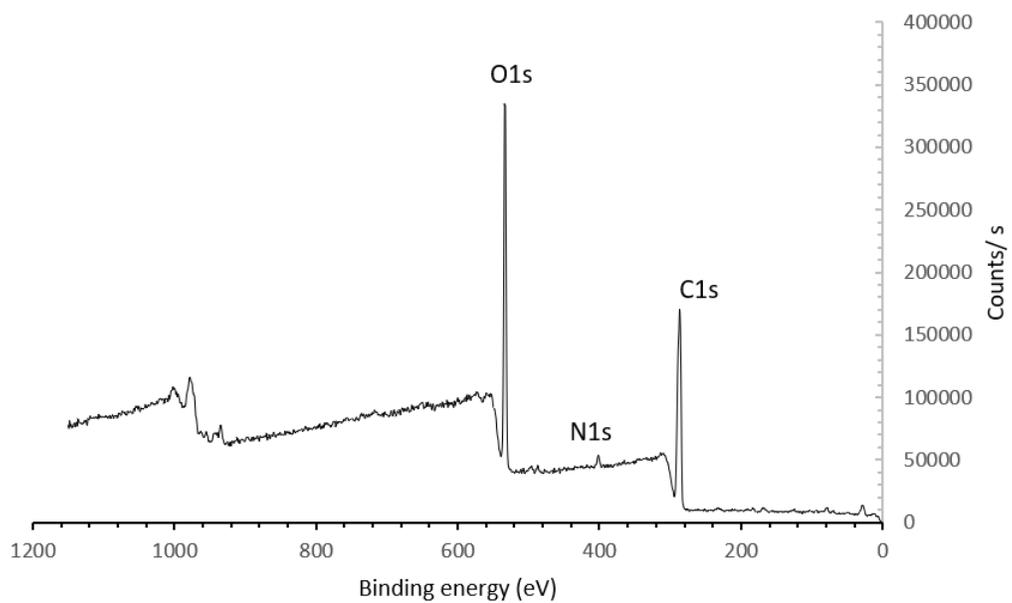
**Figure S-7.**  $^1\text{H}$  NMR spectra (300 MHz,  $\text{CDCl}_3$ ). trimethylammonium-substituted PL



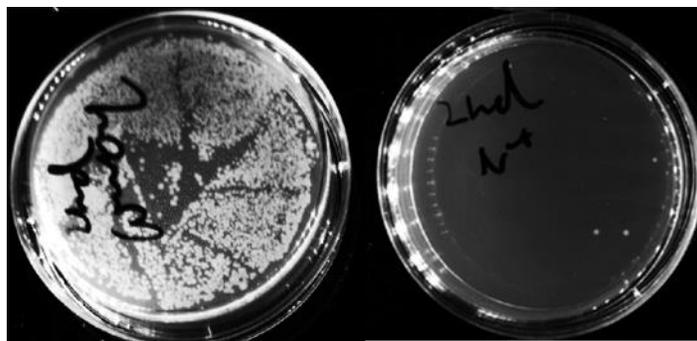
**Figure S-8.** DSC (5 °C/min, from -10 °C to 200 °C) trioctylammonium-substituted PL



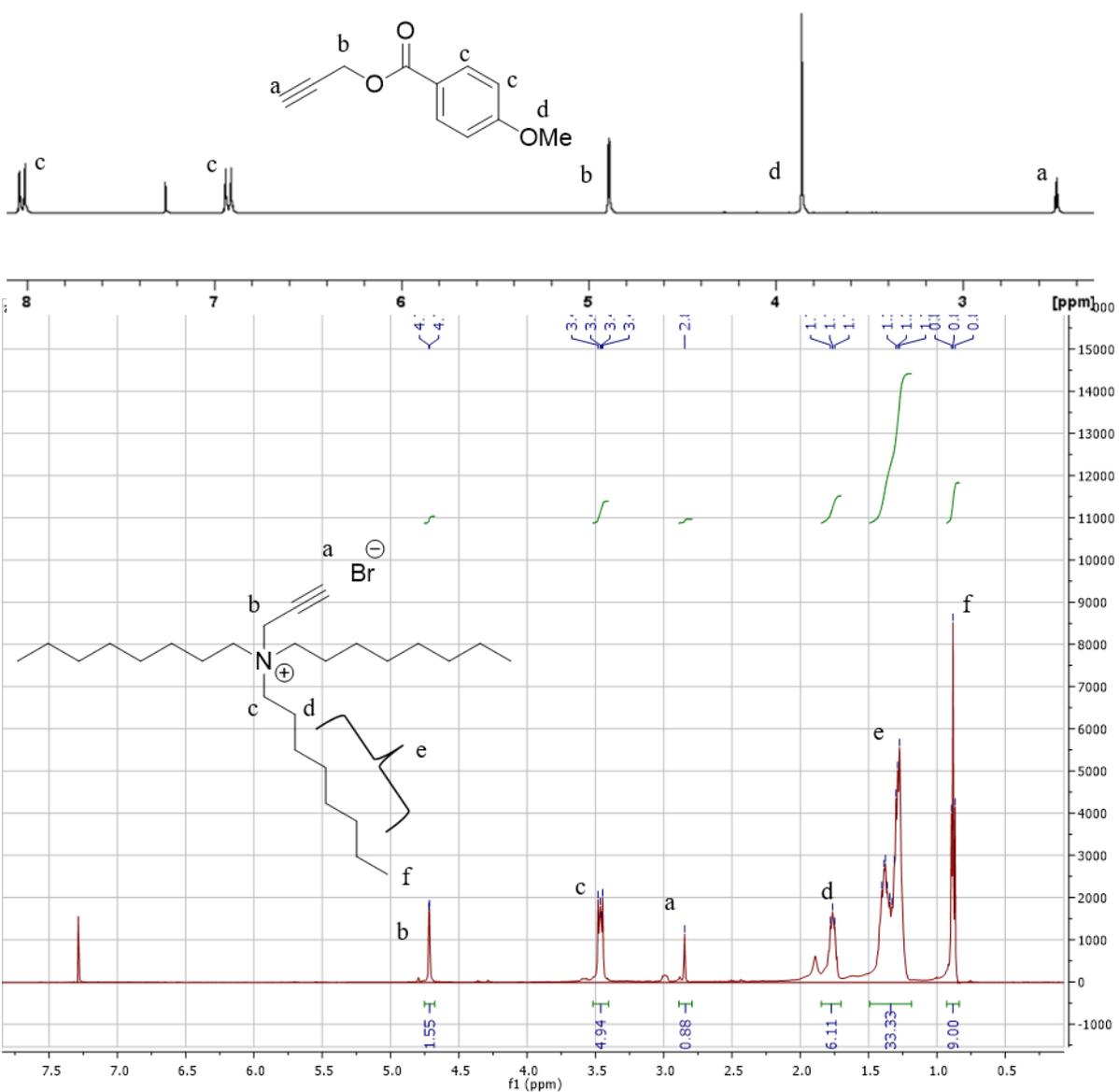
**Figure S-9.** Agar plate assays for growth inhibition of *E. coli* on treatment with the suspensions of substituted PL: A to G, increasing concentration of trioctylammonium-substituted PL; H, 2% DMSO solution, I-J trioctylpropargyl ammonium bromide; K, azido-PL; L, PBS buffer.



**Figure S-10.** XPS survey spectra of trioctylammonium-substituted PL



**Figure S-11.** Retention of antibacterial activity upon re-exposure of cationic PL film to *E. coli* suspension. Agar plate obtained post treatment of *E. coli* with control PL film (on the left) and cationic PL film (on right) used for the second time. After the first exposure to *E. coli*, the films were rinsed to remove adherent cells and re-exposed to *E. coli* suspension for 1 hour.



**Figure S-12.**  $^1\text{H}$  NMR spectra (300 MHz,  $\text{CDCl}_3$ ). Top Propargyl 4-methoxybenzoate.  $N,N,N$ -Trioctyl- $N$ -propargylammonium bromide.

## Detailed $^1\text{H}$ NMR analysis

**Azido-PL.** The  $^1\text{H}$  NMR spectrum of the precipitated copolymer shows the presence of a quartet at 5.15 ppm (signal *p*, Figure 2B) and a doublet at 1.57 ppm (signal *q*) which correspond to the methine and the methyl groups, respectively, of the lactide units of the copolymer. Four multiplets between 2.0 and 3.5 ppm (signals *b*, *c* and *d*, and *e* Figure 2B) can be assigned to the hydrogen atoms of the methylene units in the azidopropylthiomethyl side chain on the substituted-lactide units of the copolymer. Comparison of the integrals of these signals with those of the methine quartet (signals *p* and *a*) shows that the product contained 5% of the functional comonomer, which is similar to the composition of the starting ene-PL. Complete disappearance of the signals corresponding to the alkene units of ene-PL (Figure 2A) confirmed the quantitative addition of the thiol under these conditions. The spectrum of azido-PL also shows the presence of a quartet at 4.3 ppm (signal *x*, Figure 2B) that can be assigned to the methine hydrogen atom at the hydroxyl end of the copolymer.

**Propargyl-4-methoxybenzoate PL adduct.** The  $^1\text{H}$  NMR spectrum of the copolymer shows a quartet and a doublet at 5.15 and 1.57 ppm, respectively, corresponding to the  $\text{AX}_3$  spin system of the lactide unit of the copolymer, Figure 2C. Along with these peaks, the spectrum shows signals corresponding to the 4-methoxybenzoate group (2H doublets at 8.0 and 6.9 ppm, and a 3H singlet at 3.8 ppm). These peaks, in addition to the appearance of a singlet at 7.7 ppm corresponding to the triazole hydrogen, indicated the success of the cycloaddition reaction. Integration of these peaks suggested the quantitative addition of alkyne to the pendent azide group under these reaction conditions.