

## Electronic Supplemental Information

### Covalent Functionalization of Graphene Oxide with Polyesters as a Mechanically Enhanced Scaffold for Tissue Regeneration

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## Experimental Procedures

### Preparation of graphene oxide (GO)

GO was synthesized using a modified Hummer's method as we have previously reported,<sup>1</sup> although it has been slightly modified here. The entire reaction was carried out behind a blast shield: 5 g of graphite (Graphite Flakes, Natural, ~325 Mesh, 99.8%, Alfa Aesar, Ward Hill, MA, USA) and 125 mL of conc. H<sub>2</sub>SO<sub>4</sub> (Certified ACS+, Fisher Chemical, Fair Lawn, NJ, USA) were added to a 1L round bottom flask on ice with stirring. Then, 10 g of KMnO<sub>4</sub> (ACS, 99.0%, Alfa Aesar, Ward Hill, MA, USA) was added over 20-30 m. The reaction was then removed from the ice bath and allowed to warm to room temperature and continued stirring for 2 h. The reaction was then heated to 35 °C and stirred an additional 2 h. Next, the reaction was cooled in an ice bath with stirring followed by the addition of 500 mL DI H<sub>2</sub>O quickly. When the reaction was below 50 °C, 10 mL of 30% H<sub>2</sub>O<sub>2</sub> (VWR Chemicals, Radnor, PA, USA) was added over 5 m. An additional 225 mL of DI H<sub>2</sub>O was added. The reaction was stirred overnight at room temperature. Then, the reaction mixture was vacuum filtered, collected, and was directly dialyzed (SnakeSkin™, 3.5K MWCO, 35 mm Dry I.D., Thermo Scientific, Rockford, IL, USA) against DI H<sub>2</sub>O for 3-7 days until the water was clear. The water was changed twice the first day and once per day thereafter. The GO was removed from dialysis tubing and lyophilized for 3-5 days until dry. GO was characterized by TGA and FTIR before proceeding to CG synthesis.

### Preparation of Claisen graphene (CG)

GO was then modified to CG by converting the oxidized GO functional groups to carboxylic acids separated from the basal plane with a methylene bridge via the Johnson-Claisen Rearrangement.<sup>2</sup> Briefly, a flame or oven-dried 500 mL round bottom with stir bar was charged with 1.23 g of GO and 250 mL triethylorthoacetate (98%, Alfa Aesar, Heysham, LA3 2XY, England) and dispersed via sonication for 10 m under N<sub>2</sub>. Then, 21 mg of *p*-toluene sulfonic acid (Monohydrate, 98.5%, Sigma-Aldrich, St. Louis, MO, USA) was added and the reaction was refluxed at 150 °C for 36 h. The reaction was allowed to cool to room temperature and quenched with 50 mL of 1.0 M NaOH (NaOH Pellets, Certified ACS, Fisher Chemical, Fair Lawn, NJ, USA). The reaction was stirred for 3 h at room temperature. The CG was vacuum filtered and the puck was collected and the supernatant discarded. The CG was then washed once with acetone, three times with DI water, and twice with acetone. Each wash was separated with 3600 x G centrifugation for 5 m and the supernatant discarded. The pellet was then resuspended in 40 mL of the next solvent. After all wash steps, the CG was dried under vacuum for 48 h. CG was characterized by TGA and FTIR before proceeding to ACG synthesis.

### Preparation of acyl chloride graphene (ACG)

This CG was then converted to acyl chloride graphene (ACG) by converting the carboxylic acids to carbonyl chlorides with oxalyl chloride as previously reported.<sup>2</sup> Briefly, 50 mL of dry *p*-dioxane (DrySolv®, EMD Millipore Corp., Billerica, MA, USA) and 5 drops of dimethylformamide (GR ACS, EMD Millipore Corp., Billerica, MA, USA) were added to a flame or oven-dried round bottom with stirring. Then, 256 mg of CG was added and dispersed via sonication for 10 m. 0.7 mL of oxalyl chloride (98%, Alfa Aesar, Ward Hill, MA, USA) was added dropwise over 5 m, and the reaction was left to stir at room temperature under N<sub>2</sub> overnight. The reaction was then centrifuged for 20 m at 4,500 x G and the supernatant discarded. ACG was washed with dry acetone, centrifuged and supernatant discarded again, then dispersed in dry acetone to be added *in situ* to quench PCL, PLA, or PGA polymerizations. ACG was characterized by TGA and FTIR before use in polyester end-capping.

### Example ring-opening polymerizations using lactide and glycolide

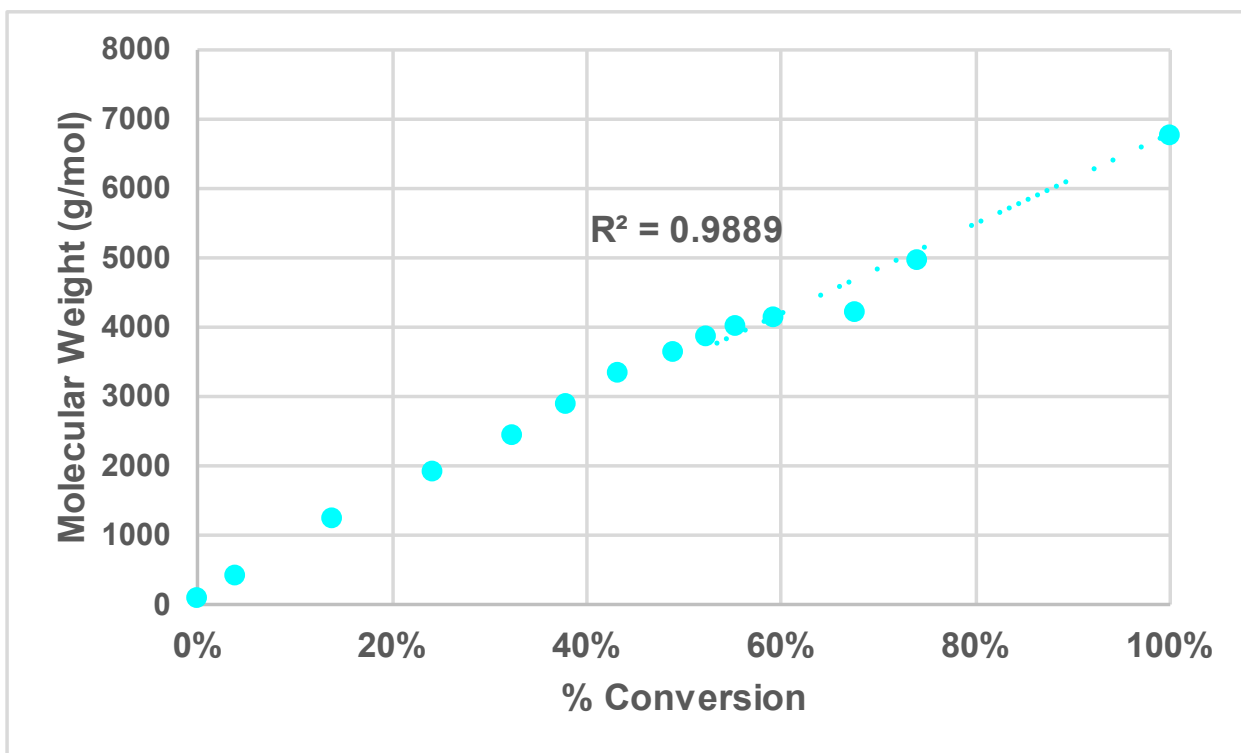
PCL, PLA, and PGA were synthesized via a living ring-opening polymerization with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 3,4,4'-Trichlorocarbaniide (TCC) coordination co-catalysts.<sup>3</sup> Polymers were characterized by gel permeation chromatography (GPC), proton-nuclear magnetic resonance (<sup>1</sup>H-NMR) spectroscopy, and x-ray photoelectron spectroscopy (XPS). The polymerizations were monitored via <sup>1</sup>H-NMR end group analysis.

In a typical PLA preparation, recrystallized TCC (1.25 mol eq.) and recrystallized racemic lactide (100 mol eq.) were dissolved in a minimal amount of dry benzene. DBU (1.25 mol eq.) and dry benzyl alcohol (1 mol eq.) were combined separately and added together. All glassware was thoroughly dried by oven prior to use and proper Schlenk technique with dry nitrogen was used in all steps. Benzene and benzyl alcohol were dried under 4Å sieves. TCC and lactide were recrystallized in dry acetone and dry ethyl acetate, respectively. After stirring for 4-8 h at 50 °C, the polymerization was quenched with 1:1 w/w ACG:lactide *in situ* in minimal amount of dry acetone. For example, if 1 g of lactide monomer was added for the polymerization, 1 g of ACG was used to quench. The P-CG product was washed separately with 40 mL of hexane, methanol, and THF and separated by 3600xg centrifugation for 5 m each. The supernatants were discarded, apart from THF, which then 10x v/v hexane was added to precipitate PLA for analysis.

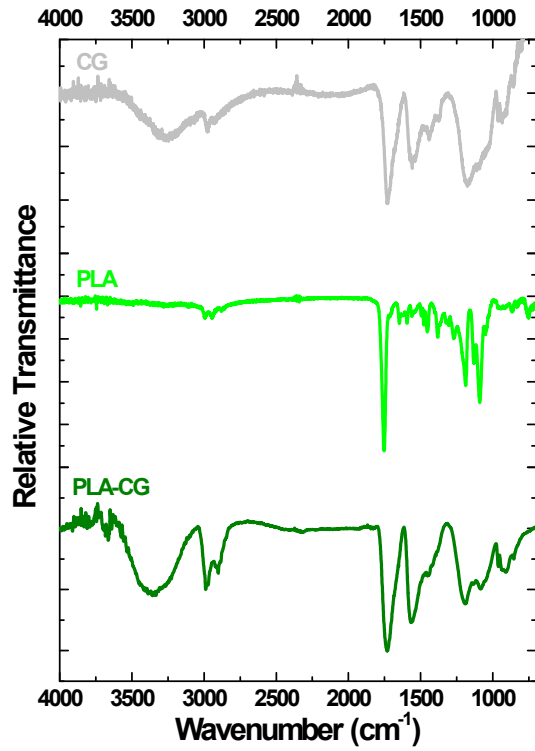
In a typical PGA preparation, recrystallized TCC (1.25 mol eq.) and glycolide (100 mol eq.) were dissolved in a minimal amount of dry *p*-dioxane. Glycolide remained dispersed until the addition of DBU. DBU (1.25 mol eq.) and dry benzyl alcohol (1 mol eq.) were combined separately and added together. All glassware was thoroughly dried by oven prior to use and proper Schlenk technique with dry N<sub>2</sub> was used in all steps. DrySolv® *p*-dioxane was used and benzyl alcohol was dried under 4Å sieves. TCC was recrystallized in dry acetone. After stirring for 4-8 h at 50 °C, the polymerization was quenched with 1:5 w/w ACG:glycolide *in situ* in dry acetone. For example, if 5 g of glycolide monomer was added for the polymerization, 1 g of ACG was used to quench. The P-CG product was washed separately with 40 mL of hexane, methanol, and trifluoroacetic acid and separated by 3600xg

centrifugation for 5 m each. The supernatants were discarded, apart from trifluoroacetic acid, which then 10× v/v hexane was added to precipitate PGA for analysis.

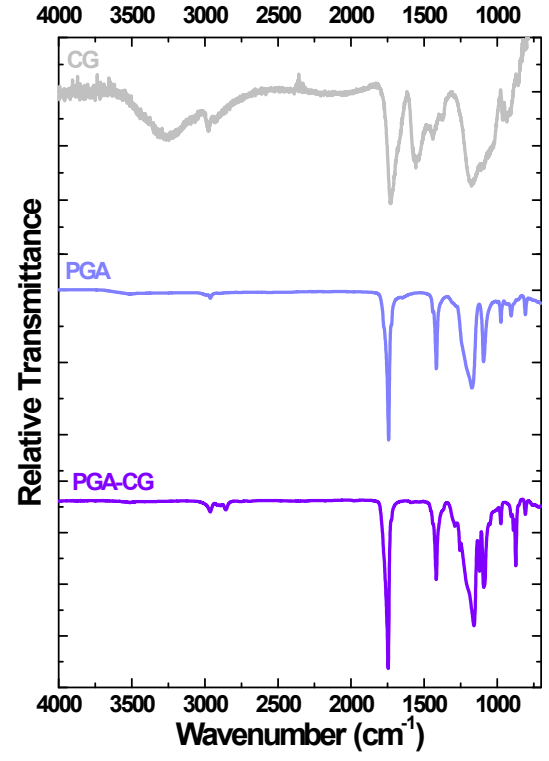
## Figures, Results and Discussion



**Figure S1.** Linear fit of molecular weight to percent conversion of PCL monitored by  $^1\text{H-NMR}$  over 24 h.



**Figure S2.** FTIR functional group comparison of polylactic acid-Claisen graphene (PLA-CG) and components.



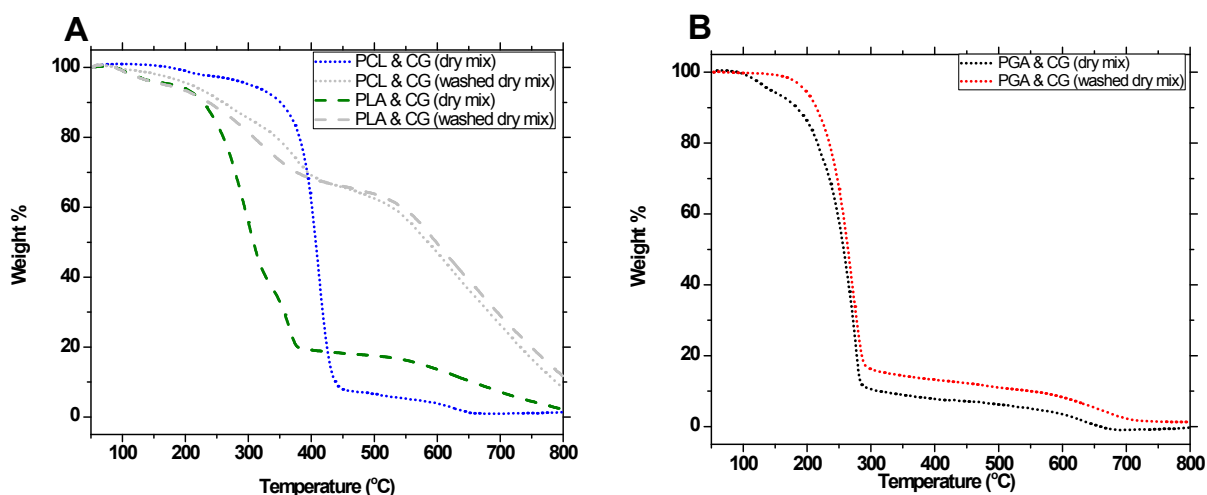
**Figure S3.** FTIR functional group comparison of polyglycolic acid-Claisen graphene (PGA-CG) and components.

The temperature and magnitude of weight loss in TGA thermograms suggests covalent conjugation of polyesters to CG (Figure S4). Covalently attached PCL can be identified through a distinct weight loss pattern with an onset temperature of approximately 380 °C. A similar pattern is seen without washing a non-covalent dry mix of PCL and GO. However, when compared to a washed non-covalent mixture, no degradation event is seen at 380 °C; the thermogram of a washed non-covalent mixture parallels that of GO due to the absence of the large polyester degradation event.

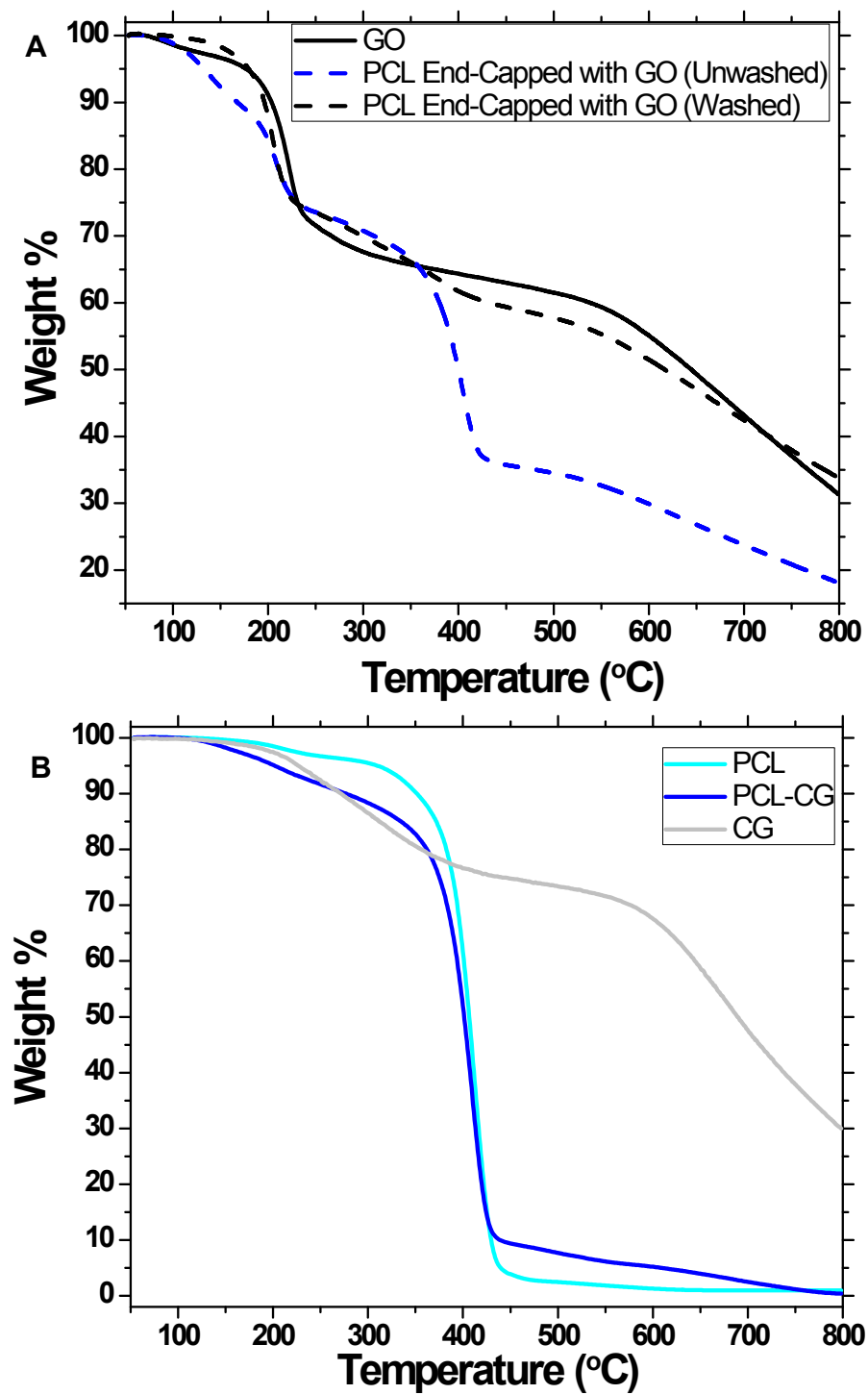
Further, we can confirm that the electrophilic acid chlorides of ACG are necessary for polyester functionalization of graphene. When the polymerization is quenched with GO rather than ACG, no attachment is observed, as when the mix of GO and PCL is treated with tetrahydrofuran (THF), all the PCL dissolves; after decanting the THF, only GO remains. When PCL-CG is treated with THF, only excess, unreacted PCL is removed.

Additionally, we provide evidence for covalent attachment and proof of the effectiveness of the washing method by utilizing the solubility of PCL and PLA in THF. When a dry mix of CG and PCL or PLA is washed with the THF, the adsorbed polymer is efficiently and fully removed. Conversely, when the P-CG materials are washed with the relevant solvent, the polymer remains on the graphenic backbone, thus supporting covalent attachment (Figure S5).

<sup>1</sup>H-NMR spectra for PGA were obtained using deuterated trifluoroacetic acid (TFA). PGA is sufficiently soluble in TFA to obtain reliable spectra that can be used for end-group analysis. However, PGA is only sparingly soluble, and as a result, is insufficient for complete washing of PGA-CG. This suggests that excess PGA strongly adsorbs onto the surface of PGA-CG, demonstrating that these materials can be used to create strong covalent and non-covalent composites with polyesters. As an additional measure to attempt to separate adsorbed PGA with CG, a dry mix of PGA and CG was dialyzed in 3.500 kDa MW cutoff tubing, as the highest calculated MW average for PGA was 3.242 kDa. However, due to the limited solubility of PGA in H<sub>2</sub>O and the strong adsorption of PGA onto PGA-CG, dialysis was ineffective at cleansing PGA-CG from excess adsorbed PGA.



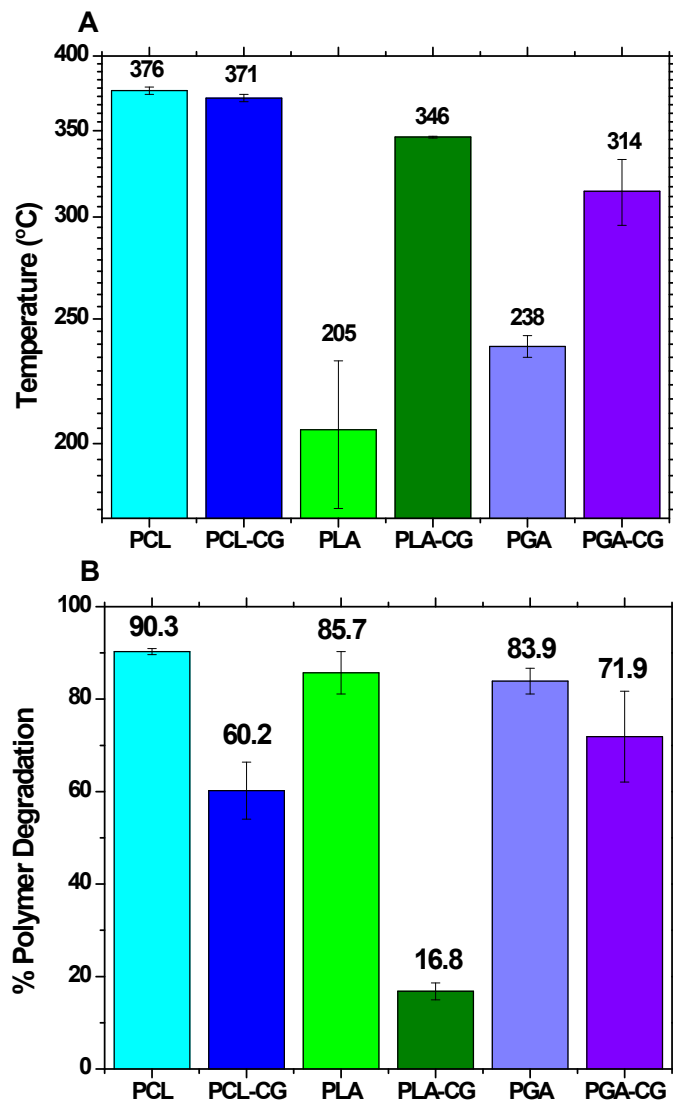
**Figure S4.** TGA overlays of dry mixes before and after washings. **A**, PCL (powder) was mixed with CG (powder) 10:1 w/w then tested on TGA. Then the mix was washed once with THF, and tested on TGA again. PLA (solid) was mixed with CG (powder) 1:1 w/w then tested on TGA in similar manner to PCL. Both PCL and PLA tests show successful washing out of adsorbed polymer, as both materials post-THF wash give a similar degradation thermogram to CG (Fig S5B). **B**, PGA (powder) was mixed with CG (powder) 5:1 w/w then tested on TGA in a similar manner to PCL and PLA, except the PGA and CG dry mix was washed with *p*-dioxane. This solvent was chosen as it is the most effective at dissolving the monomer, glycolide, and no solvents were found to effectively dissolve PGA. The washing procedure was ineffective, even when washed repeatedly and with different solvents. This is owed to PGA's apparent limited solubility and adsorption affinity for the graphenic backbone.



**Figure S5.** **A**, (top) When polymers are end-capped with GO, we don't see covalent attachment to GO that retains polymer after a THF wash. **B**, (bottom) TGA thermogram comparisons of PCL and PCL-CG. Covalent attachment is suggested as PCL remains on CG even after THF washing.

We can identify the polyester attached to and quantify the composition of the P-CGs using the relative weight percent of each degradation event. We quantify the polymer degradation events in TGAs of isolated polymer samples as well as the P-CG material the polymer was isolated from (Figure S6).

For the cases of PLA-CG and PGA-CG, functionalizing the material appears to increase the polymer degradation temperature a different amount from each material. PCL-CG shows no significant difference, PLA shows an increase of approximately 76 °C, while PGA shows the highest increase of approximately 141 °C. An increase may be due to the ineffectiveness of the heat transfer from the TGA pan to the sample from covalent conjugation. This enhanced thermal stability may prove useful in processing for future applications for this technology. PCL appears to be an exception to this observation, which may be explained by PCL's higher effective heat capacity compared to PLA and PGA.<sup>4-6</sup> The higher heat capacity may overshadow the effects of covalent conjugation on the degradation temperature.



**Figure S6.** Numerical figures on TGA data. **A**, Temperature at which the polymer degrades in °C. **B**, Sample's weight % lost to degradation of the polymer. For example, PCL-CG experienced a 60.2% weight % loss at 371 °C, which is attributed to the PCL in PCL-CG.

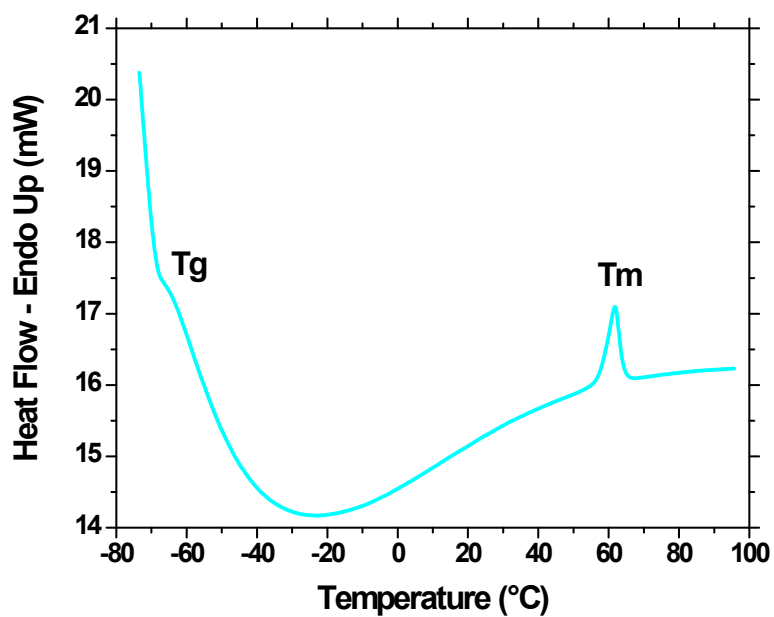


The appropriate weight percent ratios of ACG to polyester are summarized below (Table S1). “<5:1” is report for PGA, as excess PGA strongly adsorbs onto PGA-CG, as described in the ESI (ESI pg. S5). Therefore, the exact functionalization ratio was

	<b>Determined Ratio</b>	
	<b>(Polymer:ACG) Ratio to Use</b>	
<b>PCL-CG</b>	6:1	10:1
<b>PLA-CG</b>	1:2.5	1:1
<b>PGA-CG</b>	<5:1	5:1

**Table S1.** Calculated w/w ratios of polyester to ACG to achieve an efficient P-CG synthesis. “Ratio to Use” represents the appropriate synthetic ratio for P-CG formulations.

undetected.



**Figure S7.** Differential scanning calorimetry (DSC) of excess unreacted PCL isolated from PCL-CG synthesis. The second temperature sweep is exclusively shown, as volatiles appear in the first temperature sweep. The glass transition temperature ( $T_g$ ) can be seen at approximately  $-60$  °C as a kink in the thermogram, which is caused by a change in heat capacity. The melting temperature ( $T_m$ ) can be seen at approximately  $60$  °C with a spike, which is caused by absorption of heat during melting. The absence of a crystallization temperature ( $T_c$ ) is due to the amorphous nature of PCL.

**Survey Scans:** Three survey scan spectra were acquired for each material at different spot locations to prevent artifacts from sample degradation due to the x-ray source. Spectra were collected using 5 cumulative scans per spectrum, over a binding energy range of 1350 to -10 eV, a pass energy of 150 eV, a dwell time of 10 ms, and an energy step size of 1 eV. Quantification of elemental composition from survey scans was performed in CasaXPS software (CasaXPS) by integrating the area under the peaks, where peaks are unique for each element. A smart background correction and a standard peak type were used for each element quantified. Oxygen, nitrogen, carbon, and chlorine were quantified using the O1s, N1s, C1s, and Cl2p emission peaks, respectively.

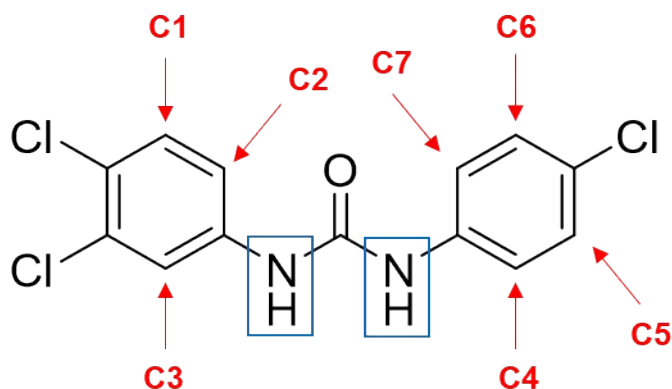
**High Resolution Carbon Scans:** High resolution C1s scans were collected using 10 cumulative scans per spectra, a pass energy of 50 eV, a dwell time of 50 ms, and an energy step size of 0.1 eV. The spectra were smoothed in OriginPro (OriginLab) using Savitzky–Golay smoothing (second–order polynomial with a window of 45). Spectra were corrected to the adventitious carbon peak at 284.8 eV and truncated to 29–281 eV. Then, spectra were then Shirley background subtracted and deconvoluted using Gaussian peak fitting using Fityk (Version 0.9.8). All peaks were constrained to a full-width-at-maximum of 1.4 eV. See Table S2 for additional peak fitting parameters for all materials.

Nitrogen and chlorine are unique atoms to the 3,4,4'-Trichlorocarbanilide (TCC) catalyst used for the polyester polymerizations. Nitrogen and chlorine content were identified in the survey scans of the polymers PCL and PLA, indicating the presence of trace amounts of the TCC catalyst. Considering this, TCC contains chemically distinct carbon functional groups, which contribute to the area under the curve of the C1s spectra for polycaprolactone and polylactic acid; polyglycolic acid was free of catalyst impurities. Thus, separating the TCC signal from the polymer signal in the high resolution C1s spectra was necessary to evaluate the degree of polymerization.

#### **Correcting the C-C/C=C Signal**

The nitrogen atomic percent determined for the survey scans was used to subtract the TCC contribution from the C-C/C=C signal. First, the chemical structure of TCC was considered, as shown below. There are seven carbon atoms, labelled with red arrows, that contribute to the C-C/C=C peak in the high resolution C1s spectra for every two nitrogen atoms, boxed in blue, which yields a 7:2 carbon to nitrogen ratio.

## TCC Catalyst Chemical Structure



The C-C/C=C peak area was normalized to the total carbon atomic percent determined from survey scans using the following equation:

$$\text{Equation S1. Normalized C - C/C = C At.\%} = \left( \frac{\text{C - C/C = C Peak Area}}{100} \right) * (\text{Carbon At.\%})$$

Then, the carbon signal from TCC in the C-C/C=C peak was subtracted from the total C-C/C=C, yielding only the carbon signal of the polymer in the C-C/C=C peak:

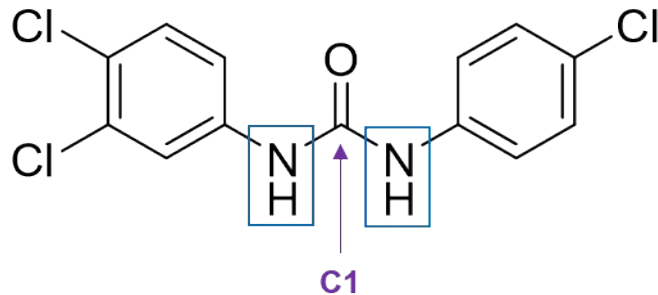
$$\text{Equation S2. Corrected C - C/C = C At.\%} = \text{Normalized C - C/C = C At.\%} - \text{Nitrogen At.\%} * \left( \frac{7 \text{ Carbon Atoms}}{2 \text{ Nitrogen Atoms}} \right)$$

Note that the carbon and nitrogen atomic percent used in Equations S1 and S2 were from the survey scan data that was collected on one spot as the high resolution C1s spectrum, rather than an average atomic percent from all three survey scan spectra.

### Correcting the O-C=O Signal

The nitrogen atomic percent determined for the survey scans was also used to subtract the TCC contribution from the O-C=O signal. Again, the chemical structure of TCC was considered. There is one carbon atom, labelled with a purple arrow, that contributes to the O-C=O peak in the high resolution C1s spectra for every two nitrogen atoms, boxed in blue, in the molecule, which yields a 1:2 carbon to nitrogen ratio.

## TCC Catalyst Chemical Structure



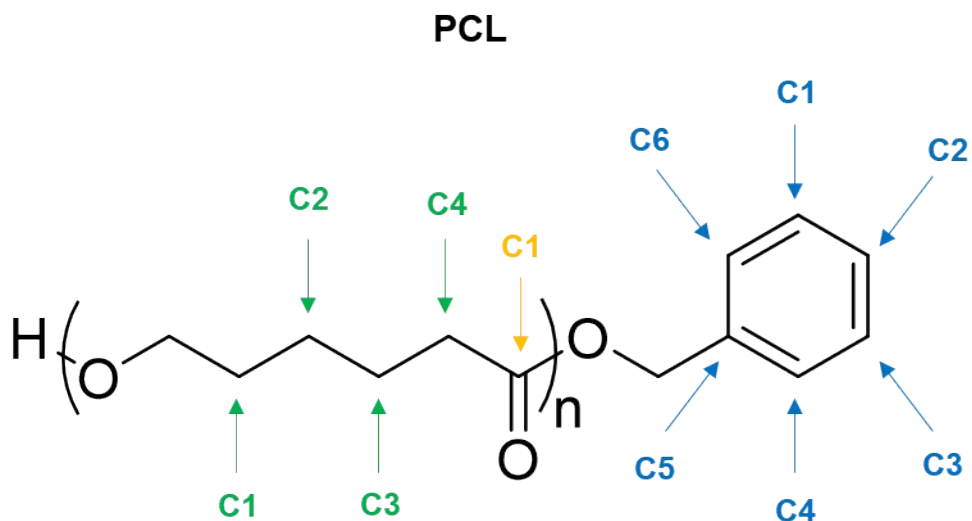
The O-C=O peak area was normalized to the total carbon atomic percent determined from survey scans, using the same approach demonstrated in Equation S1. Then, the carbon signal from TCC in the O-C=O peak was subtracted from the total O-C=O, yielding only the carbon signal of the polymer in the O-C=O peak. This calculation was conducted using an equation similar to Equation S2 using the one carbon atom to two nitrogen atoms ratio.

### Polyester Degree of Polymerization (DP) Determination

The DP of each polymer was determined using a modified, end-group analysis technique. The chemical structure of the polymers and the corrected area under the curves of the deconvoluted C1s spectra (calculated using Equations S1 And S2) were utilized for DP calculations.

#### PCL DP

The chemical structure of PCL is shown below. PCL contains 4 carbon atoms in each repeat unit (designated by green arrows) that contribute to the C-C/C=C signal and 1 carbon atom in each repeat unit (designated by an orange arrow) that contributes to the O-C=O signal in the high resolution C1s spectrum. However, it must be noted there are also 6 carbon atoms from the benzyl end Group, indicated by blue arrows, that contribute to the C-C/C=C signal.



The average degree of polymerization for PCL was determined using Equation S3. That is, the signal from the carbon atoms of the end group can be isolated by subtracting the total C-C/C=C signal (end group + backbone signal) from the O-C=O signal (backbone signal). Note that the O-C=O is multiplied by 4 due to the 4 to 1 ratio of C-C/C=C carbon atoms to O-C=O carbon atoms in each repeat unit. The resulting difference yields the carbon signal from each benzyl end group. Next, the ratio of the O-C=O signal (which is 1 carbon atom per repeat unit) to the C-C/C=C signal of the benzyl end group (6 carbon atoms per end group) can be used to calculate the average degree of polymerization.

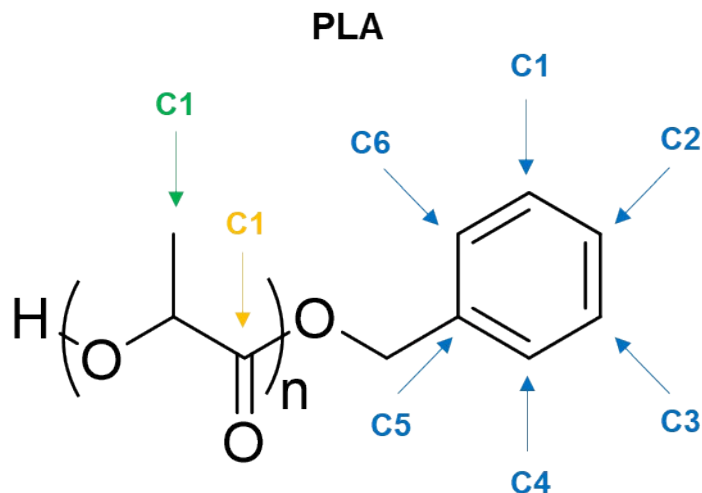
$$\text{Equation S3. PCL DP} = \frac{6 * (\int O - C = O)}{(\int C - C / C = C) - [4 * (\int O - C = O)]}$$

#### PLA DP

The chemical structure of PLA is shown below. PLA contains one carbon atom in each repeat unit, designated by a green arrow, that contribute to the C-C/C=C signal and one carbon atom in each repeat unit, designated by an orange

arrow, that contributes to the O-C=O signal in the high resolution C1s spectrum.

There are also six carbon atoms from the benzyl end group, indicated by blue arrows, that contribute to the C-C/C=C signal.



The average degree of polymerization for PLA was determined using

Equation S4. The signal from the carbon atoms of the end group can be

isolated by subtracting the total C-C/C=C signal (end group + backbone signal)

from the O-C=O signal (backbone signal). The resulting difference yields the

carbon signal from each benzyl end group. Next, the ratio of the O-C=O signal

(which is 1 carbon atom per repeat unit) to the C-C/C=C signal of the benzyl end

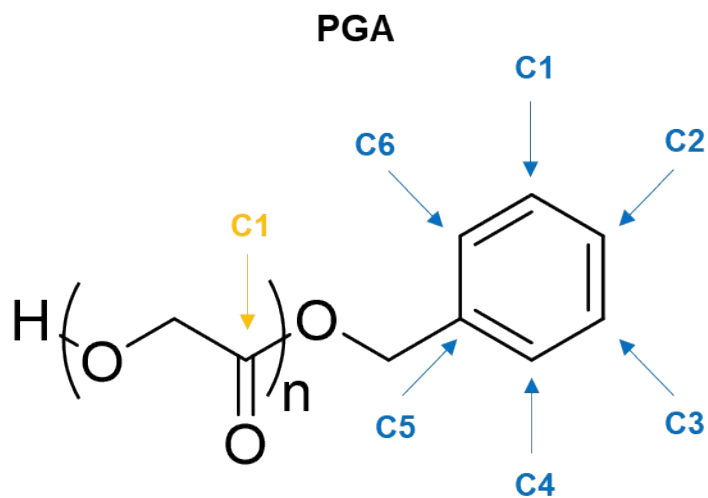
group (6 carbon atoms per end group) can be used to calculate the average degree of polymerization.

$$\text{Equation S4. PLA DP} = \frac{6 * (\int \text{O-C=O})}{(\int \text{C-C/C=C} - \int \text{O-C=O})}$$

#### PGA DP

The chemical structure of PGA is shown below. The only contribution to

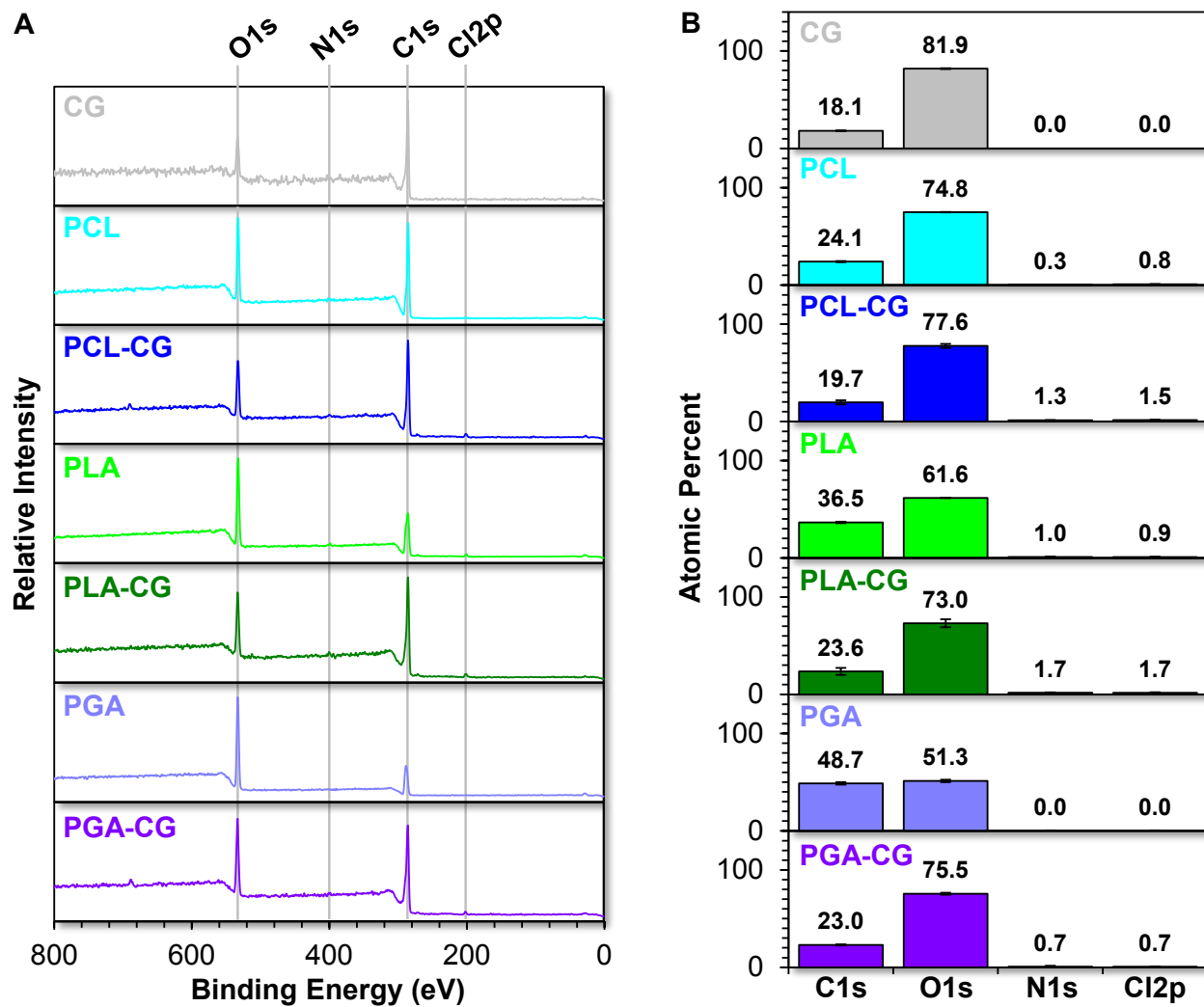
the C-C/C=C signal in the high resolution C1s spectrum is from the carbon atoms in the benzyl end group of each polymer chain (indicated by blue arrows). PGA also contains 1 carbon atom in each repeat unit (designated by an orange arrow) that contributes to the O-C=O signal in the high resolution C1s spectrum.



The average degree of polymerization for PGA was determined using Equation S5. the ratio of the O-C=O signal (which is 1 carbon atom per repeat unit) to the C-C/C=C signal of the benzyl end group (6 carbon atoms per end group) can be used to calculate the average degree of polymerization.

$$\text{Equation S5. PGA DP} = \frac{6 * \int \text{O-C=O}}{\int \text{C-C/C=C}}$$





**Figure S8a.** Elemental analysis using X-ray photoelectron spectroscopy (XPS) of Claisen graphene (CG), polycaprolactone (PCL), polylactic acid (PLA), polyglycolic acid (PGA), and PCL-CG, PLA-CG, and PGA-CG composites. **A**, XPS survey scan spectra and **B**, elemental analysis in atomic percent obtained from the survey spectra in panel **A**.

Survey Scan	Atomic % C	Atomic % N
PCL	74.6%	0.8%
PLA	61.7%	1.4%
PGA	52.0%	0.0%

**Figure S8b.** Exact atomic percent values obtained from elemental analysis of neat polyesters.

<b>Table S2. High Resolution XPS Peak Fitting of C1s Spectra</b>					
		<b>O-C=O</b>	<b>C=O</b>	<b>C-O</b>	<b>C-C/C=C</b>
<b>CG</b>	Peak Center (eV)	289.0	287.4	286.5	284.8
	Area Under Curve (At.%)	6.0	5.9	18.5	69.6
<b>PCL</b>	Peak Center (eV)	288.7	0.0	286.1	284.7
	Area Under Curve (At.%)	15.4	0.0	20.1	64.6
<b>PCL-CG</b>	Peak Center (eV)	288.7	287.4	286.1	284.7
	Area Under Curve (At.%)	13.2	0.7	19.0	67.1
<b>PLA</b>	Peak Center (eV)	288.7	0.0	286.7	284.7
	Area Under Curve (At.%)	28.7	0.0	32.5	38.8
<b>PLA-CG</b>	Peak Center (eV)	289.1	287.5	286.3	284.8
	Area Under Curve (At.%)	9.3	8.1	16.2	66.3
<b>PGA</b>	Peak Center (eV)	289.1	0.0	286.7	284.6
	Area Under Curve (At.%)	46.9	0.0	46.8	6.3
<b>PGA-CG</b>	Peak Center (eV)	289.2	287.4	286.2	284.8
	Area Under Curve (At.%)	12.9	11.2	17.9	58.0

**Table S3. Carboxylic Acids Functionalized with Polyesters (%)**

<b>PCL-CG</b>	<b>PLA-CG</b>	<b>PGA-CG</b>
12.0 %	0.1 %	0.9 %

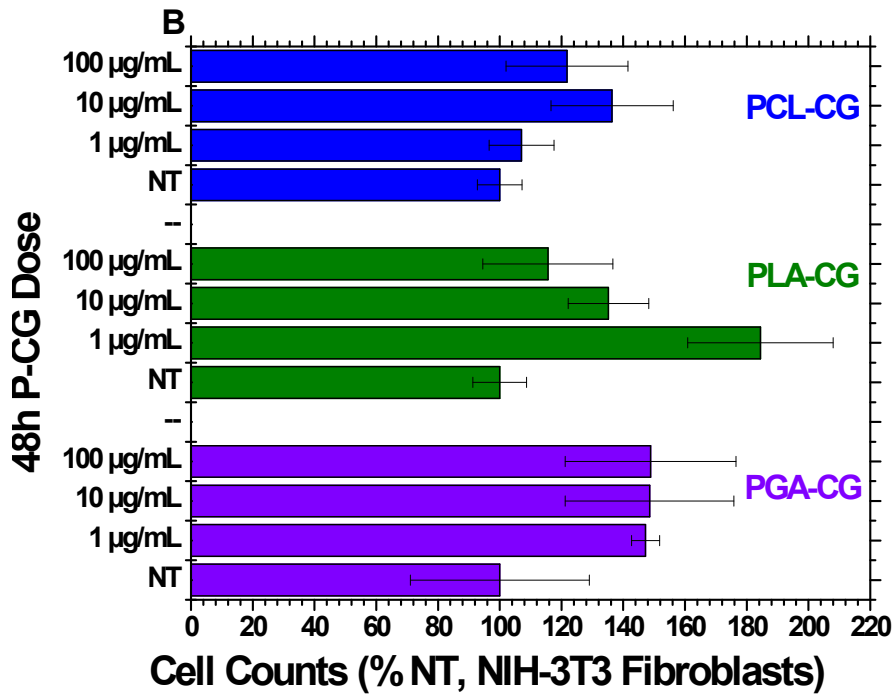
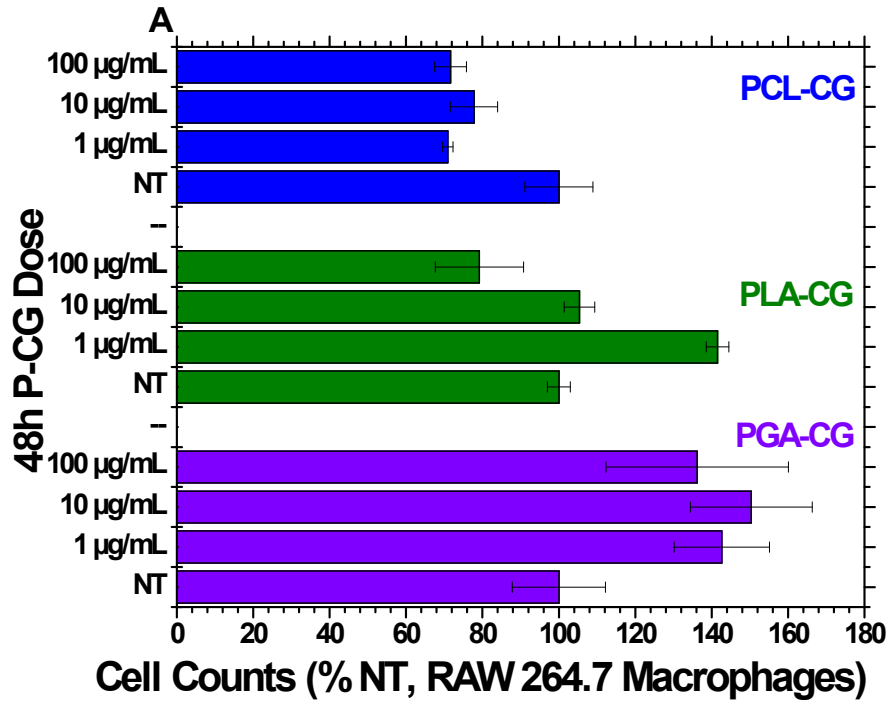


Figure S9. Cell counts after 48 h exposure to P-CGs as a NT % (A, RAW 264.7 Macrophages and B, NIH-3T3 Fibroblasts). Error bars represent SEM of technical triplicates.

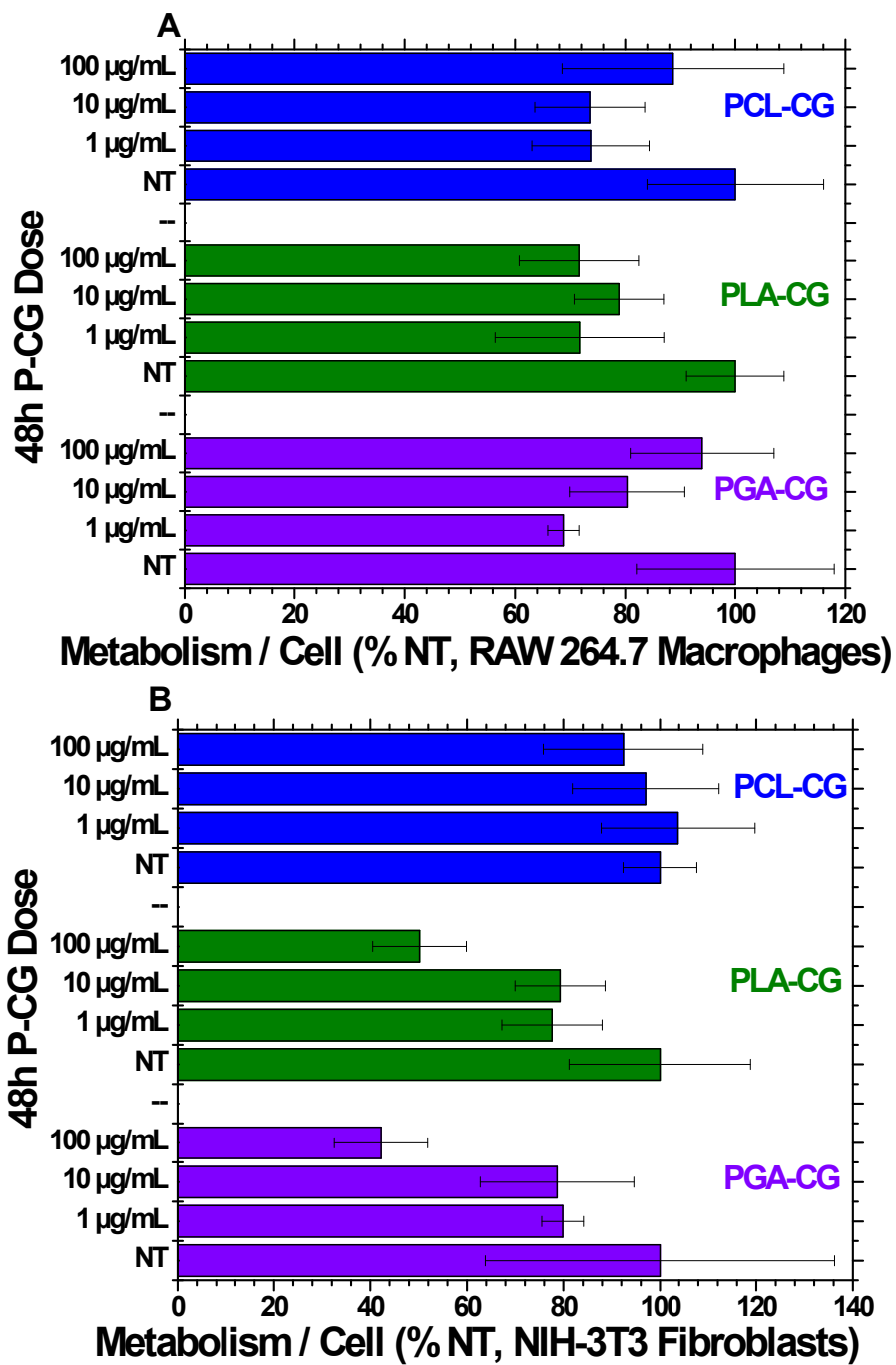
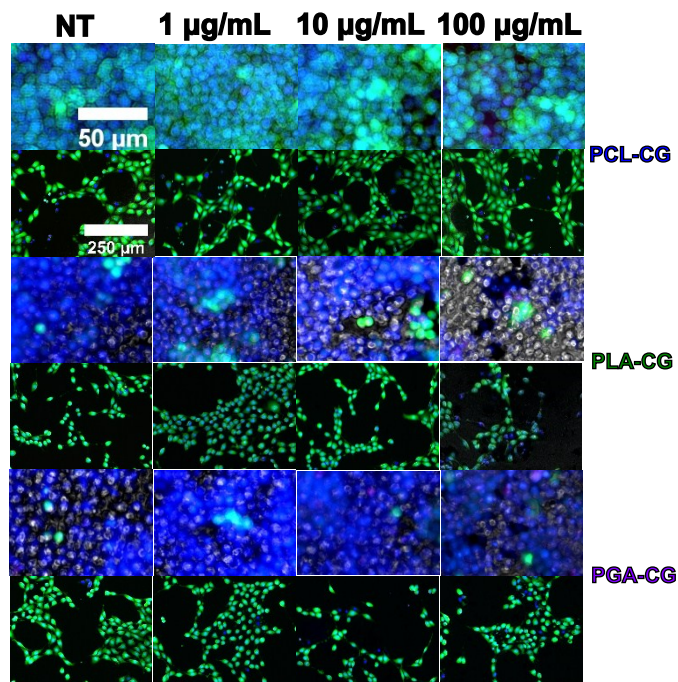
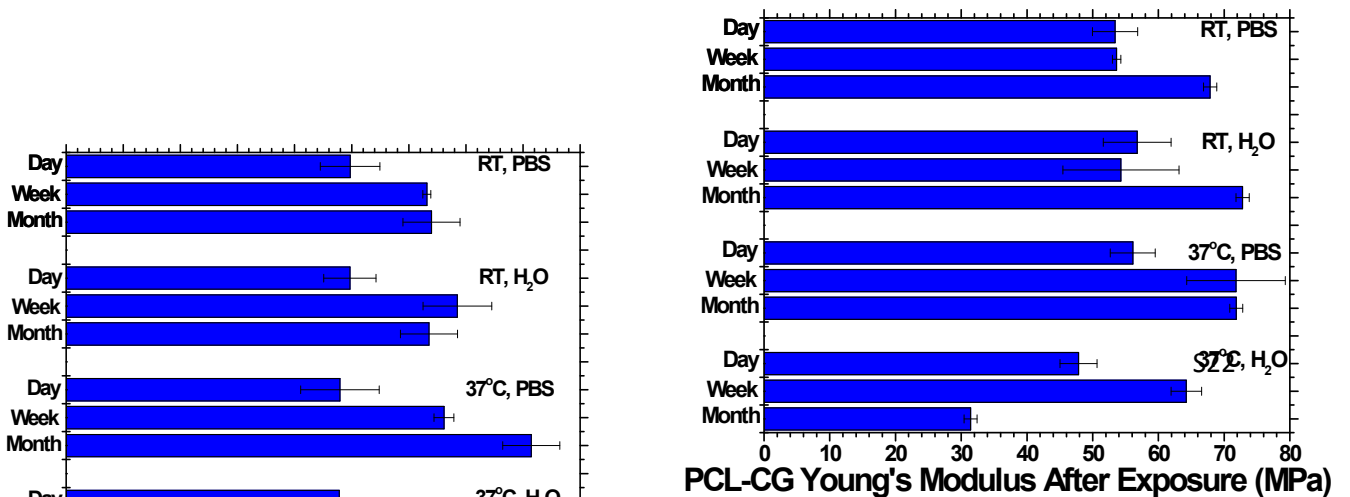


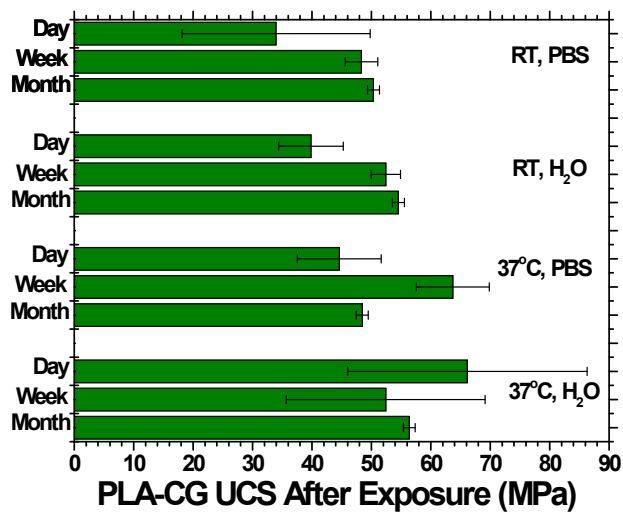
Figure S10. Cell metabolism after 48 h exposure to P-CGs as a NT % (A, RAW 264.7 Macrophages and B, NIH-3T3 Fibroblasts). Error bars represent SEM of technical triplicates.



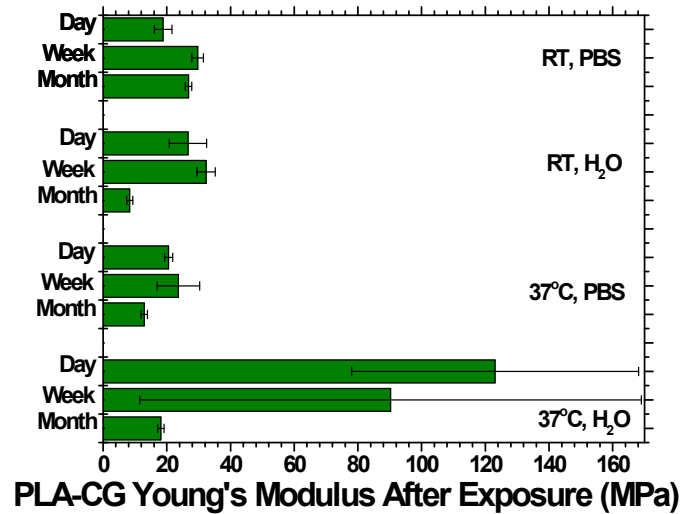
**Figure S11.** Cell fluorescence overlay images. The top row of each material shows each P-CG in the presence of RAW 264.7 macrophages, while each bottom row shows P-CGs in the presence of NIH-3T3 fibroblasts. The scale bars apply to all cells of each respective cell line. The columns are organized by concentration as indicated at the top of each column. Calcein AM (green) and Hoechst 33342 (blue) fluorophores used for assessing metabolic activity and as a DNA label, respectively. Propidium iodide (red) fluorophore labels the DNA of dying cells.



**Figure S13.** Young's modulus of PCL-CG after a day, week, or month in DI water or PBS at room temperature or 37 °C. Error bars represent SEM of technical triplicates.



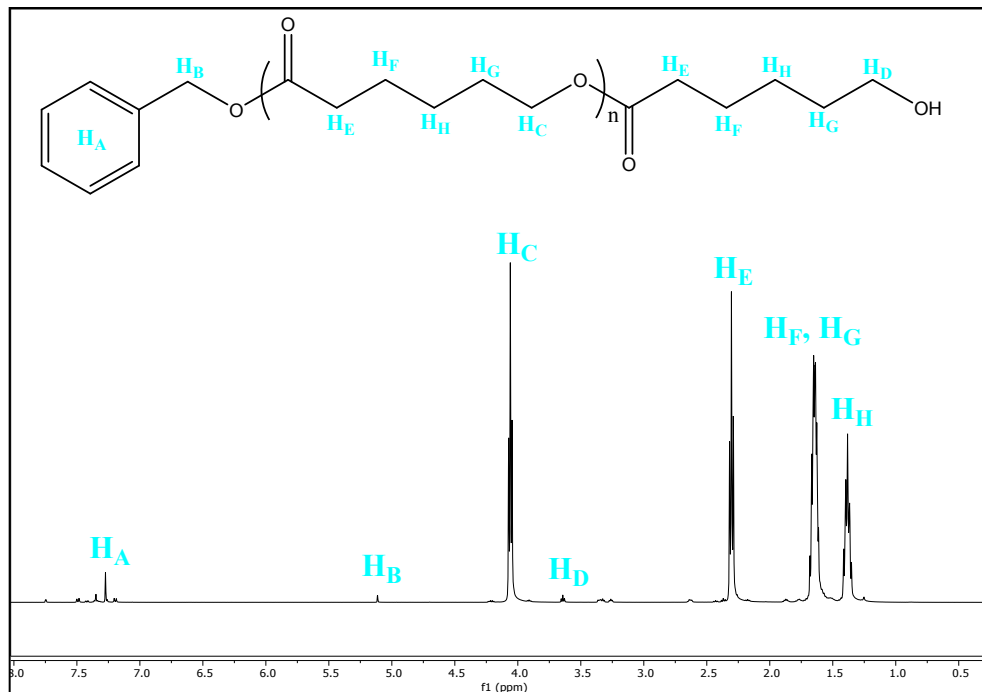
**Figure S14.** Ultimate compressive strengths of PLA-CG after a day, week, or month in DI water or PBS at room temperature or 37 °C. Error bars represent SEM of technical triplicates.



**Figure S15.** Young's modulus of PLA-CG after a day, week, or month in DI water or PBS at room temperature or 37 °C. Error bars represent SEM of technical triplicates.

Only two pellets of PGA-CG retained enough structural stability to be tested, as all others dispersed in solution. The n=1 surviving pellets were RT H<sub>2</sub>O day which had a UCS and Young's modulus of 7.60 and 11.2 MPa, respectively, as well as RT PBS day which had a UCS and Young's modulus of 8.08 and 21.5 MPa, respectively. Even the other two for each of these two treatments dispersed enough to not allow mechanical testing.

Since PGA-CG disperses easily in solution, and especially at physiological temperature, this supports tunable degradation based on the polyester.



**Figure S16.**  $^1\text{H-NMR}$  spectra of PCL were taken in  $\text{CDCl}_3$  solvent.  $\text{H}_\text{D}$  was taken as the end group reference point and normalized to an integration of 2. Starting with the aromatic region,  $\text{H}_\text{A}$  signal (which represents three non-identical aromatic proton signals) also includes  $\text{CHCl}_3$  solvent signal from proton exchange. To account for this, the strong singlet from the solvent signal was subtracted from the aromatic region, which gave a remaining integration of 4.6. This is close to the expected integration of 5.  $\text{H}_\text{B}$  and  $\text{H}_\text{C}$  had overlapping signals, but by simply subtracting 2 from the combined integration we may extract the representative integration for  $\text{H}_\text{C}$ . A similar strategy was used for  $\text{H}_\text{E}$ ,  $\text{H}_\text{F}$ ,  $\text{H}_\text{G}$ , and  $\text{H}_\text{H}$ .  $\text{H}_\text{D}$  and  $\text{H}_\text{C}$  were used for end-group analysis representing the end and chain groups, respectively. The end-group analysis equation with corresponding integrals and the result is shown below (Equation S6).

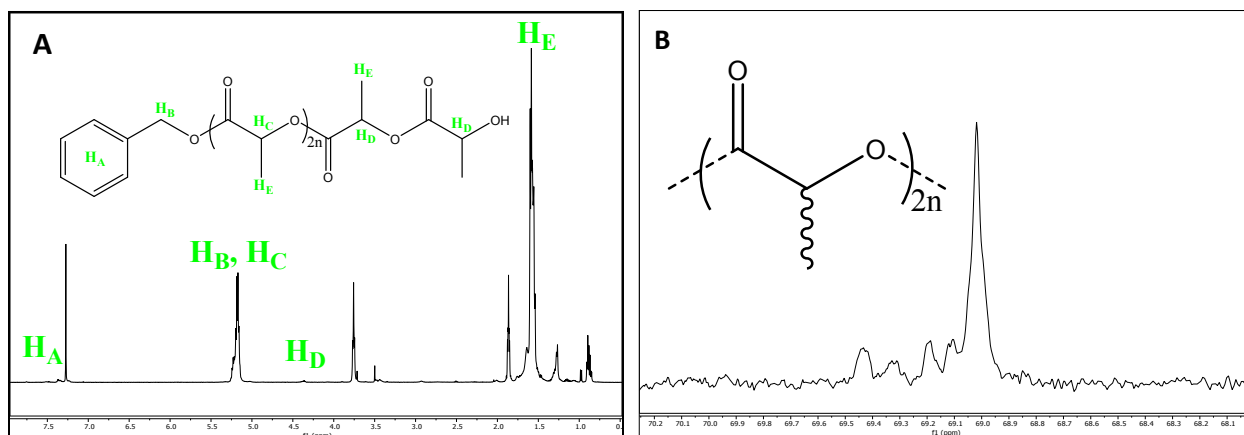
Equation S6:

$$\frac{\int H_\text{D}}{\# H_\text{D} \text{ Protons}} = \frac{(\int H_\text{C})}{(\# H_\text{C} \text{ Protons}) * DP}$$

$$\frac{2.00}{2} = \frac{(103.86)}{2 * DP}$$

$$DP = \text{Degree of Polymerization} \approx 65.43$$





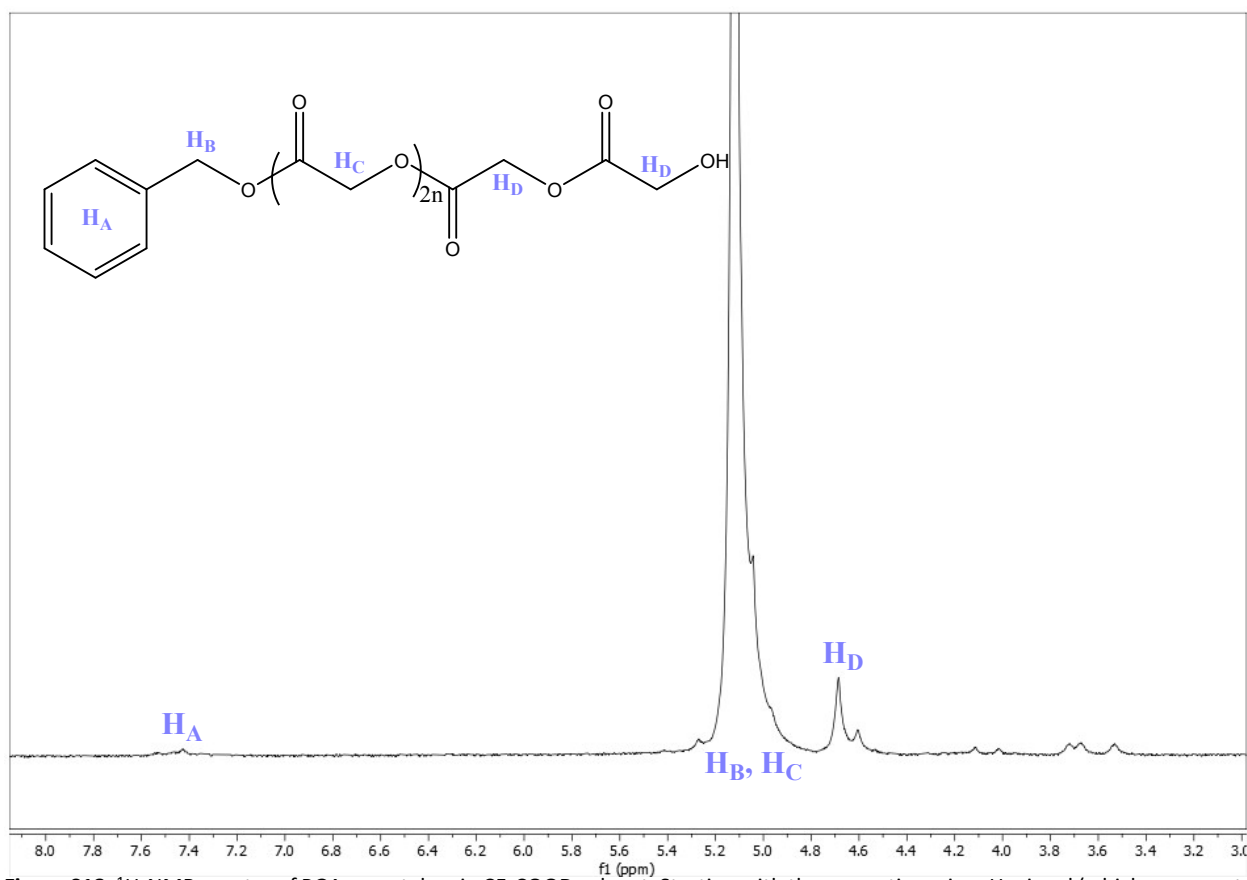
**Figure S17.** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of PLA were taken in CDCl<sub>3</sub> solvent. **A)** shows the <sup>1</sup>H-NMR spectrum with labeled corresponding proton signals. H<sub>D</sub> was taken as the end group reference point and normalized to an integration of 2. Starting with the aromatic region, H<sub>A</sub> signal (which represents three non-identical aromatic proton signals) also includes CHCl<sub>3</sub> solvent signal from proton exchange. To account for this, the strong singlet from the solvent signal was subtracted from the aromatic region, which gave a remaining integration of 5.07. This is close to the expected integration of 5. H<sub>B</sub> and H<sub>C</sub> had overlapping signals, but by simply subtracting 1 from the combined integration we may extract the representative integration for H<sub>B</sub>. A similar strategy was used for H<sub>E</sub>, but instead of subtracting 1 is it necessary to subtract 3. H<sub>D</sub> and H<sub>B</sub> were used for end-group analysis representing the end and chain groups, respectively. The end-group analysis equation with corresponding integrals and the result is shown below (Equation S7). **B)** shows a section of the <sup>13</sup>C-NMR investigating tacticity. A study of the tacticity determination via <sup>13</sup>C-NMR was recently reported.<sup>7</sup> The region of interest at approximately 69.0 ppm may be used to determine tacticity, which represents the carbon attached to H<sub>B</sub>. Our result matches exactly with their known atactic PLA; therefore, this supports our PLA as atactic. This may be explained by the monomer, which was racemic.

Equation S7:

$$\frac{\int H_D}{\# H_D \text{ Protons}} = \frac{(\int H_C) - 2}{(\# H_C \text{ Protons}) * DP * 2}$$

$$\frac{1.00}{1} = \frac{(93.2) - 2}{DP * 2}$$

$DP = \text{Degree of Polymerization} \approx 46$



**Figure S18.**  $^1\text{H-NMR}$  spectra of PGA were taken in  $\text{CF}_3\text{COOD}$  solvent. Starting with the aromatic region,  $\text{H}_\text{A}$  signal (which represents three non-identical aromatic proton signals) was taken as the end group reference point and normalized to an integration of 5.  $\text{H}_\text{B}$  and  $\text{H}_\text{C}$  had overlapping signals, but by simply subtracting 1 from the combined integration we may extract the representative integration for  $\text{H}_\text{B}$ .  $\text{H}_\text{A}$  and  $\text{H}_\text{B}$  were used for end-group analysis representing the end and chain groups, respectively. The end-group analysis equation with corresponding integrals and the result is shown below (Equation S8).

**Equation S8:**

$$\frac{\int H_\text{D}}{\# H_\text{D} \text{ Protons}} = \frac{(\int H_\text{C}) - 2}{(\# H_\text{C} \text{ Protons}) * DP * 2}$$

$$\frac{4.00}{4} = \frac{(102.27) - 2}{DP * 2}$$

$DP = \text{Degree of Polymerization} \approx 50$

<b>Acronym</b>	<b>Definition</b>
<b>ESI</b>	<b>E</b> lectronic <b>S</b> upplemental <b>I</b> nformation
<b>PCL</b>	<b>P</b> olycaprolactone
<b>PLA</b>	<b>P</b> olylactic <b>A</b> cid
<b>PGA</b>	<b>P</b> olyglycolic <b>A</b> cid
<b>GO</b>	<b>G</b> raphene <b>O</b> xide
<b>CG</b>	<b>C</b> laisen <b>G</b> raphene
<b>FGM</b>	<b>F</b> unctional <b>G</b> raphenic <b>M</b> aterial
<b>FDA</b>	<b>F</b> ood and <b>D</b> rug <b>A</b> dmistratation
<b>HA</b>	<b>H</b> ydroxyapatite
<b>ACG</b>	<b>A</b> cy l <b>C</b> hloride <b>G</b> raphene
<b>P-CG</b>	<b>P</b> olyester- <b>C</b> laisen <b>G</b> raphene
<b>GPC</b>	<b>G</b> el <b>P</b> ermeation <b>C</b> hromatography
<b>NMR</b>	<b>N</b> uclear <b>M</b> agnetic <b>R</b> esonance
<b>XPS</b>	<b>X</b> - <b>R</b> ay <b>P</b> hotoelectron <b>S</b> pectroscopy
<b>NT</b>	<b>N</b> o <b>T</b> reatment
<b>DMA</b>	<b>D</b> ynamic <b>M</b> echanical <b>A</b> nalysis
<b>ASTM</b>	<b>A</b> merican <b>S</b> ociety for <b>T</b> esting and <b>M</b> aterials
<b>DNA</b>	<b>D</b> eoxyribonucleic <b>A</b> cid
<b>UCS</b>	<b>U</b> ltimate <b>C</b> ompressive <b>S</b> trength
<b>DBU</b>	<b>1,8-Diazabicyclo[5.4.0]undec-7-ene</b>
<b>TCC</b>	<b>3,4,4'-T</b> richlorocarbanilide
<b>FT-IR</b>	<b>F</b> ourier <b>T</b> ransform- <b>I</b> nfrared <b>S</b> pectroscopy
<b>TGA</b>	<b>T</b> hermogravimetric <b>A</b> nalysis
<b>DLS</b>	<b>D</b> ynamic <b>L</b> ight <b>S</b> cattering
<b>DSC</b>	<b>D</b> ifferential <b>S</b> canning <b>C</b> alorimetry

**Table S4. Table of Acronyms**

## References

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