Electronic Supplementary Material (ESI) for Polymer Chemistry.

Suppoting Information

Nucleobase-Functionalized Supramolecular Polymer Films with Tailorable Properties and Tunable Biodegradation Rates

Chih-Chia Cheng,[a]* Jyun-Jie Huang,[a] Zhi-Sheng Liao,[a] Shan-You Huang,[a] Duu-Jong Lee,[b,c,d] and Zhong Xin[e]

[a.] Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 10607, Taiwan. E-mail: cccheng@mail.ntust.edu.tw

[b.] Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan.

[c.] Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan.

[d.] R&D Center for Membrane Technology, Chung Yuan Christian University, Chungli, Taoyuan 32043, Taiwan.

[e.] State Key Laboratory of Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China.

Experimental Section

Materials

All chemicals and reagents were analytical grade or the highest quality commercially available from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification unless otherwise specified. All solvents used in this work were high-performance liquid chromatography grade and obtained from TEDIA (Fairfield, OH, USA). Poly(ε-caprolactone) (PCL) was purchased from Sigma-Aldrich and used without further purification. Size exclusion chromatography (SEC) analysis indicated the average molecular weight of PCL was approximately 14,000 g/mol, with a polydispersity index (PDI) of 1.4. The L929 mouse fibroblast cell line was purchased from the Bioresource Collection and Research Center (Hsinchu, Taiwan).

Characterization

Proton nuclear magnetic resonance (^{1}H-NMR). ^{1}H-NMR spectra were recorded on a Varian Inova-400 MHz magnetic resonance spectrometer (Palo Alto, CA, USA). Approximately 20 mg of sample dissolved in deuterated chloroform was analyzed at 20 °C. *Size exclusion chromatography (SEC)*. Weight-average molecular weight (M_w), number-average molecular weight (M_n) and polydispersity index (PDI, M_w/M_n) were measured using a Waters 410 GPC system equipped with a refractive index detector and three Ultrastyragel columns (100, 500, 1000 Å) connected in series; dimethylformamide was the eluent and the flow rate was 0.6 mL/min. The SEC was calibrated using narrow polystyrene (PS) standards (Polymer Standards Service, Silver Spring, MD, USA). *Small-angle X-ray scattering (SAXS)*. SAXS experiments were performed at the BL17A1 beamline of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. An X-ray beam with a diameter of 0.5 mm and wavelength (λ) of 1.1273 Å was used to record SAXS data in the 0.1-2.0 nm^{-1} q range. The samples used for SAXS experiments were sealed between two Kapton windows (thickness: 12 μm) and analyzed at 25 °C. *Wide-*

Angle X-ray Diffraction (WAXD). WAXD spectra for powders were obtained at 25 °C using a Rigaku D/max-2500 X-ray diffractometer with Ni-filtered Cu Kα radiation, operated at 30 kV and 200 mA. Radiation with a wavelength of 0.154 nm was used. All test samples were measured mounted on sample holders; the diffraction data were collected in a 2θ range of 5–45° at a scan rate of 2° min^{-1}. *Differential scanning calorimetry (DSC).* DSC was performed using a PerkinElmer DSC 4000 instrument (Beaconsfield, Buckinghamshire, UK) operated at a scan rate of 10 °C/min from -50 to 150 °C. The second heating curves for each sample are shown in **Figure 3a**. *Tensile Tests.* Tensile tests were conducted using a universal testing machine (EZ-L; Shimadzu Corp, Kyoto, Japan) at 25 °C and approximately 50% relative humidity under a constant strain rate of 10.0 mm/min.

Preparation of PCL-U/PCL-triA films

PCL-U/PCL-triA films were prepared by a solvent casting method using chloroform as a solvent. PCL-triA [0.075 g (5.32×10^{-5} mol) or 0.15 g (1.06×10^{-4} mol)] was mixed with 0.4 g (1.06×10^{-5} mol) of PCL-U in 10 mL chloroform with stirring at ambient temperature for 1 day, then filtered through a membrane filter (pore size, 0.45 μm) under conventional pressure filtration. Subsequently, the blended films were prepared by casting the sample solution onto clean polytetrafluoroethylene substrate, followed by air-drying and vacuum annealing at 60 °C.

Enzymatic degradation

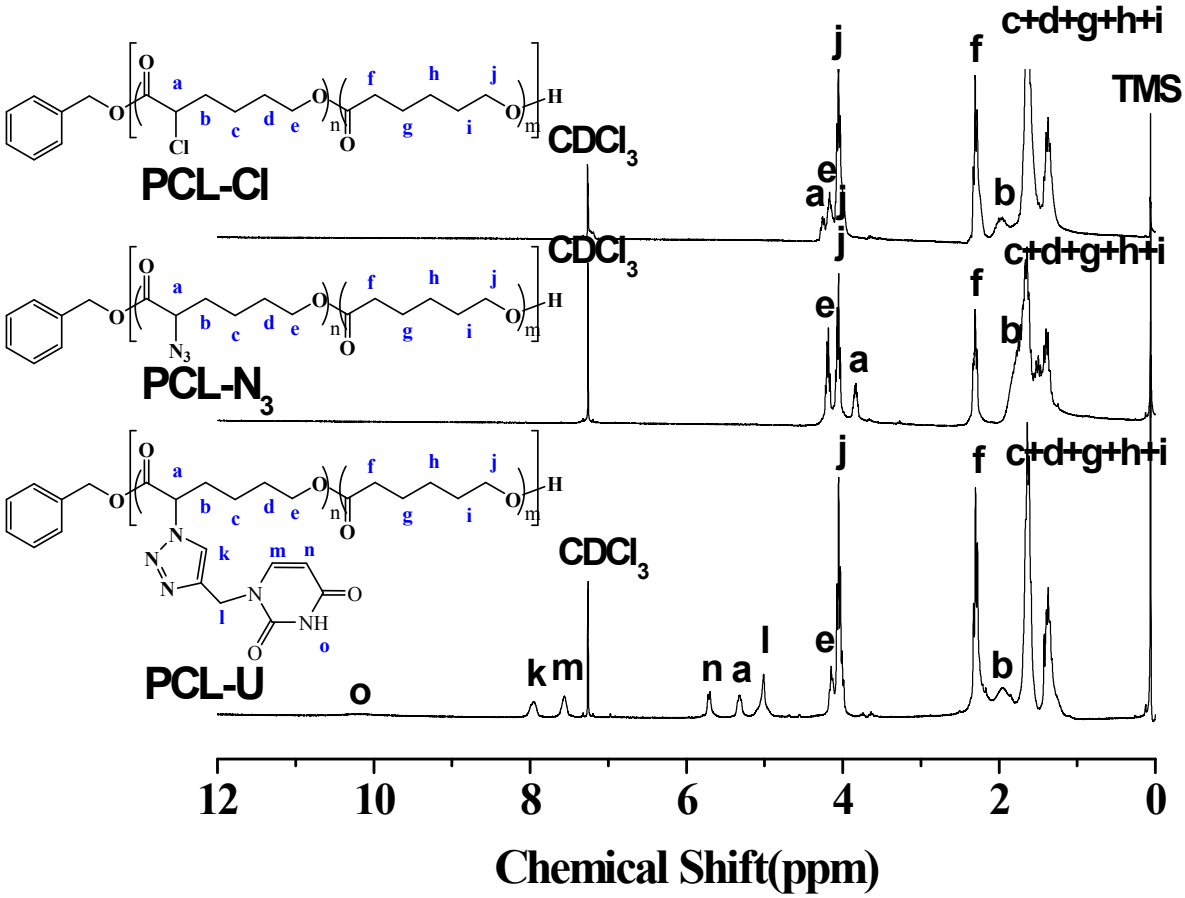
Enzymatic degradation studies for all samples were performed using a lipase from *Pseudomonas* sp (PS lipase; Amano Enzymes, Troy, VA, USA) in phosphate buffered saline (PBS) at pH 7.4 and 37 °C for 4 days. Approximately 15 mg samples were placed in closed bottles containing 10 ml of PBS, then PS lipase was added at a final concentration of 1 mg/ml. Percentage sample degradation was assessed by SEC to determine the reduction in M_w during degradation.

Cell culture

L929 cells were cultured in Dulbecco's modified Eagle's medium (DMEM) supplemented with 10% fetal calf serum (Mediatech, Fairfax, VA, USA), 1% penicillin-streptomycin and 1% geneticin selective antibiotic (Invitrogen, Carlsbad, CA, USA), and maintained in a humidified atmosphere of 5% CO_2 at 37 °C.

Evaluation of cell survival and proliferation on supramolecular films

L929 cell growth was assessed on PCL, 1/5 and 1/10 PCL-U/PCL-triA films using an optical microscope, and the numbers of adherent cells were counted in ten randomly selected fields at 10x magnification under an inverted microscope (Nikon Eclipse TE2000, Nikon, Tokyo, Japan); the experimental procedures are described in detail in our previous study.[34]



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ig. S1: The ^{1}H NMR spectra for PCL-Cl, PCL-N_3 and PCL-U in deuterated chloroform at 20 °C.

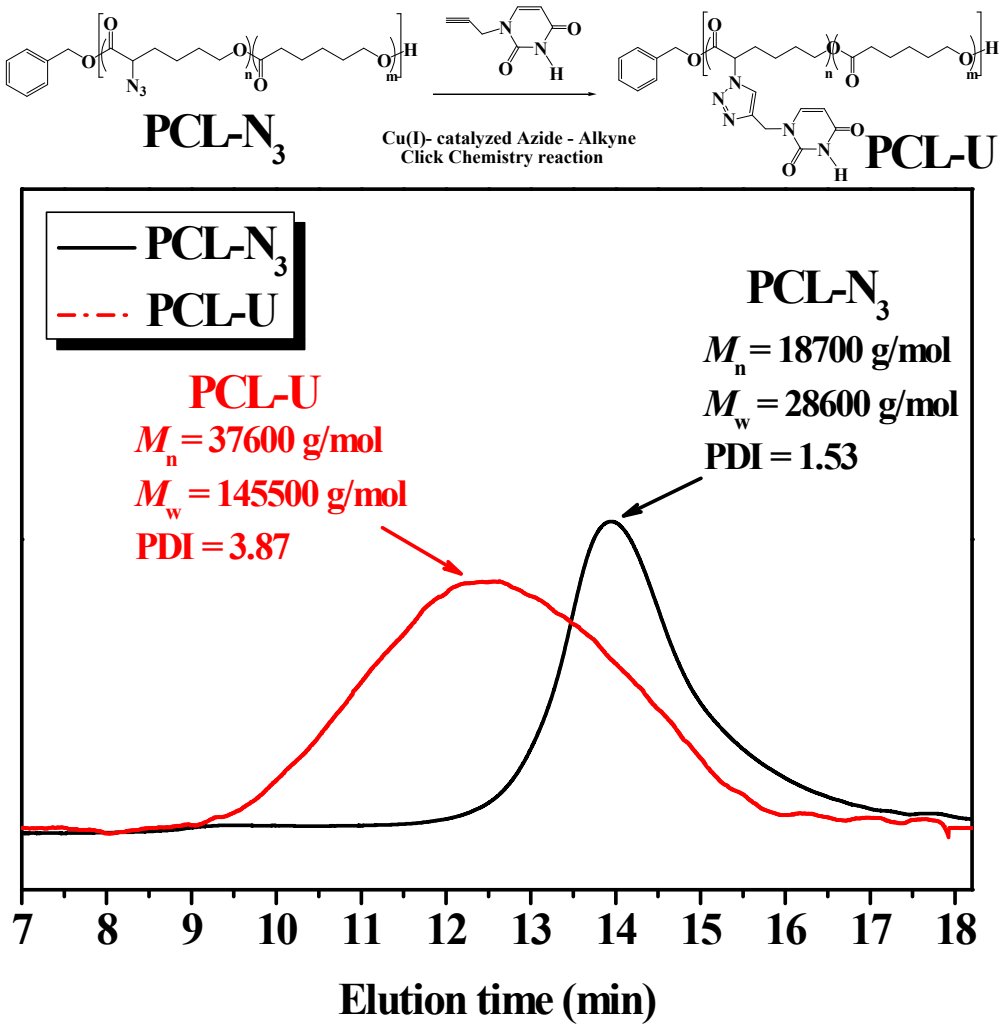

Fig. S2: SEC traces for PCL-N_3 and PCL-U.

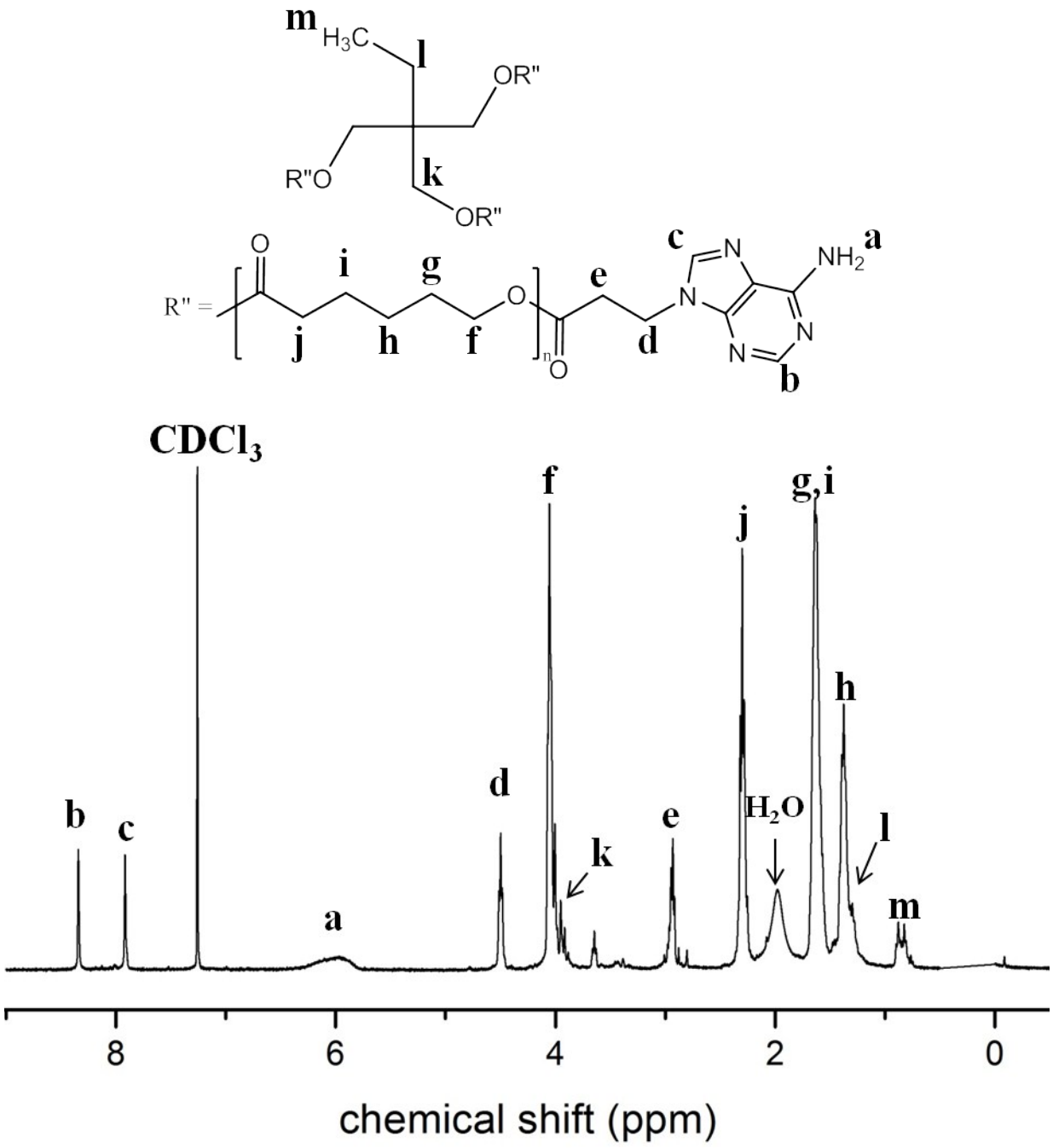

Fig. S3: ^{1}H NMR spectrum of PCL-triA in deuterated chloroform at 20 °C.

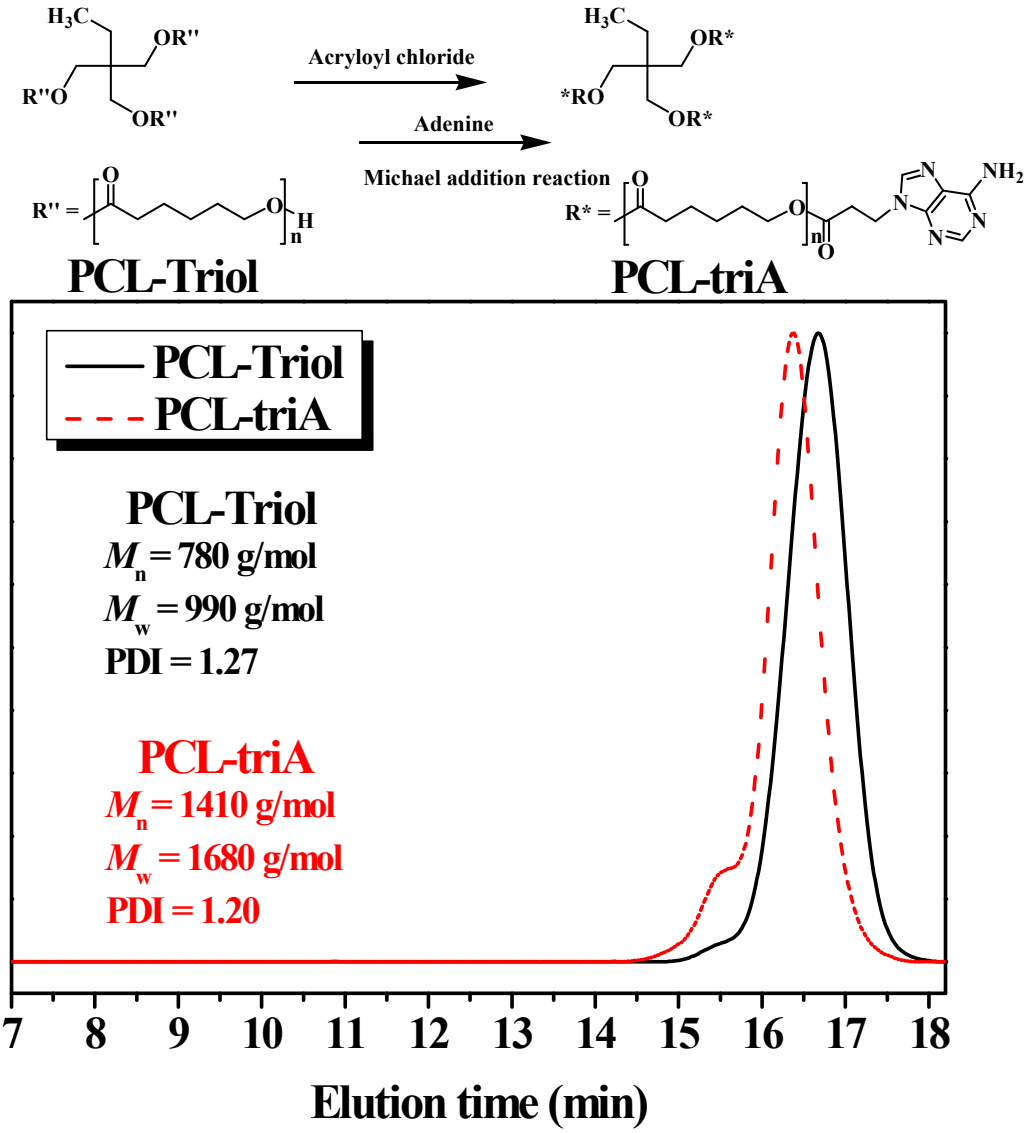

Fig. S4: SEC traces for PCL-Triol and PCL-triA.

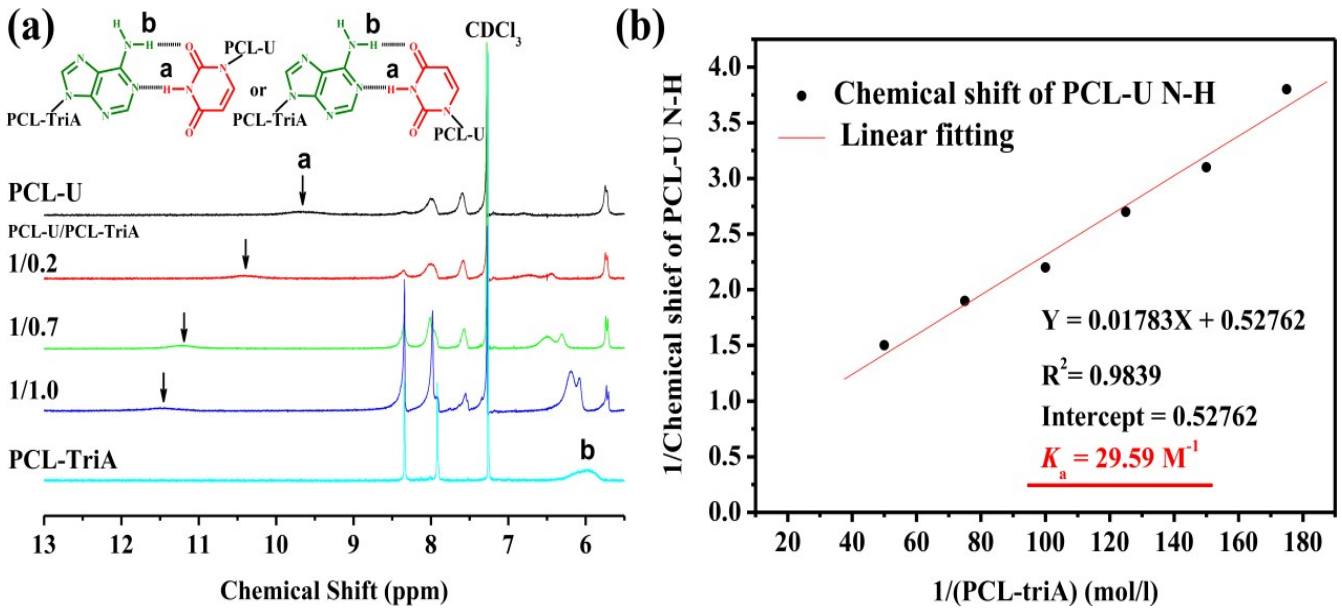

Fig. S5: (a) The ^{1}H NMR spectra and **(b)** Benesi–Hildebrand plots obtained from ^{1}H NMR titration assays of PCL-U/PCL-triA blends in deuterated chloroform at 20 °C. The N-H region of the ^{1}H NMR spectrum of PCL-U/after the addition of PCL-triA is indicated.