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可交联且可生物降解的高分子膜

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Cross-Linkable Yet Biodegradable Polymer Films

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1 Materials

2-Chlorocyclohexanone (98%) was purchased from Kaixin Chemical, *m*-Chloroperoxybenzoic acid (MCPBA) (75%), cinnamoyl chloride (97%) and Sn(II) 2-ethylhexanoate [Sn(Oct)$_2$] (95%) were supplied by Aladdin Industrial. Propargyl alcohol (99%) was obtained from Silworld Chemical. Sodium azide (analytical reagent (AR)) was supplied by IFT Chem & Tech. *α*-Chloro-*ε*-caprolactone (*α*ClCL) was prepared and purified according to the literature [1]. Isopropanol (AR) was dried with CaO and distilled under vacuum. All other reagents: triethylamine (TEA, AR), toluene (AR) and other general chemicals and solvents were supplied by Kermel Chemical Reagent and used as received.

2 Characterization

Size exclusive chromatography (SEC) was performed on a set of Agilent SEC (Agilent 1200 Series, U. S. A.) with a refractive index detector and a set of Styragel columns (Waters, U. S. A.). Tetrahydrofuran (THF) was used as eluent at a flow rate of 1.0 mL·min^{-1} and the experiments were performed at 30 °C calibrated by linear polystyrene standard. The negative peaks in the SEC curves are system peaks resulted from solvent as well as dissolved small molecules such as water or other impurities.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker 600 MHz spectrometer (Avance III, Bruker, Germany) with $CDCl_3$ as solvent at room temperature.

Fourier-transform infrared (FT-IR) spectroscopy was recorded by a Varian 600 IR (U.S.A.) spectrometer at room temperature, and samples were dissolved in CH_2Cl_2 and casted on a KBr plate for characterization.

3 Experimental Section

3.1 Synthesis of Poly(*α*-(cinnamoyloxymethyl)-1,2,3-triazol) caprolactone)$_{133}$ (PCTCL$_{133}$) and the Copolymer

The synthetic routes of PCTCL$_{133}$ and P(CL$_{156}$-*stat*-CTCL$_{28}$) are illustrated in Scheme S1. And the detailed synthetic procedures were reported in our previous literature [2].

3.2 Preparation of Polymer Films *via* Solution Casting

The procedures are illustrated in Scheme S2. The solutions of PCTCL$_{133}$ and P(CL$_{156}$-*stat*-CTCL$_{28}$) in THF (50 mg·mL^{-1}) were spread onto a clean Teflon plate, and the solvent was slowly evaporated to form polymer films of about 0.2 mm thick. The resulted films were further dried for 12 h under vacuum at 40 °C to completely remove the solvent. The PCTCL$_{133}$ film was transparent but the P(CL$_{156}$-*stat*-CTCL$_{28}$) copolymer film was translucent because the PCL segments were crystallizable.

3.3 Photocross-Linking of Polymer Films

The polymer films were exposed to an 800 W UV lamp at a fixed distance for 1 h to cross-link the cinnamate groups *via* [2 + 2] cycloaddition. Then the films were immersed into THF to investigate whether they were effectively cross-linked.

3.4 Degradation of Cross-Linked Films under Acid Catalysis

The hydrolytic degradation of materials based on PCL homopolymer need rather long time [3,4], however, the pendant groups are able to disrupt the crystallization of PCL backbones, thus significantly enhancing the degradation rate. In this research since the material is hydrophobic, the acid-catalyzed degradation of the films were studied in THF [5]. Un-cross-linked PCTCL$_{133}$ and cross-linked PCTCL$_{133}$ films were added into 0.12 mol·L^{-1} HCl/THF solution and stirred continuously. SEC test was conducted after stirring for 2 h for un-cross-linked PCTCL$_{133}$ film. For the cross-linked PCTCL$_{133}$ film, the SEC test was carried out until the bulk sample completely dissolved.

3.5 Computer Simulations

Computer simulations were performed with the software of Materials Studio 2017 [6]. The forcefield used during the whole simulation procedure was Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) II (version 1.2). During the dynamics simulations process, different ensembles can be generated and used, depending on which state variables (number of particles N, pressure P, temperature T, and volume V) are kept fixed. A variety of structural, energetic, and dynamic properties can then be calculated from the averages or the fluctuations of these quantities over the ensemble generated. The constant-temperature, constant-volume ensemble (NVT) is obtained by controlling the thermodynamic temperature and volume. The constant-temperature, constant-pressure ensemble (NPT) allows control over both the temperature and pressure. In both ensembles, the number of particles is conserved.

Herein, the method of molecular dynamics was used to simulate the formation of polymer films during solution casting and to calculate the Young's modulus of the final model film. First, the module of Amorphous Cell was used to incorporate optimized model polymers (5 PCTCL$_{10}$) into a cell. The initial densities were set to 0.010, 0.050, 0.10, 0.50, 0.70 and 1.0 g·cm^{-3}, respectively. And the cells were reconstructed to obtain their corresponding statistical total energy data. Then, successive dynamics simulations of NVT and NVP were performed on the amorphous cells by using the module of Forcite to simulate the gradual formation of the film *via* solution casting. Finally, Young's modulus of each cell was obtained with the mechanical properties calculation under the module of Forcite.

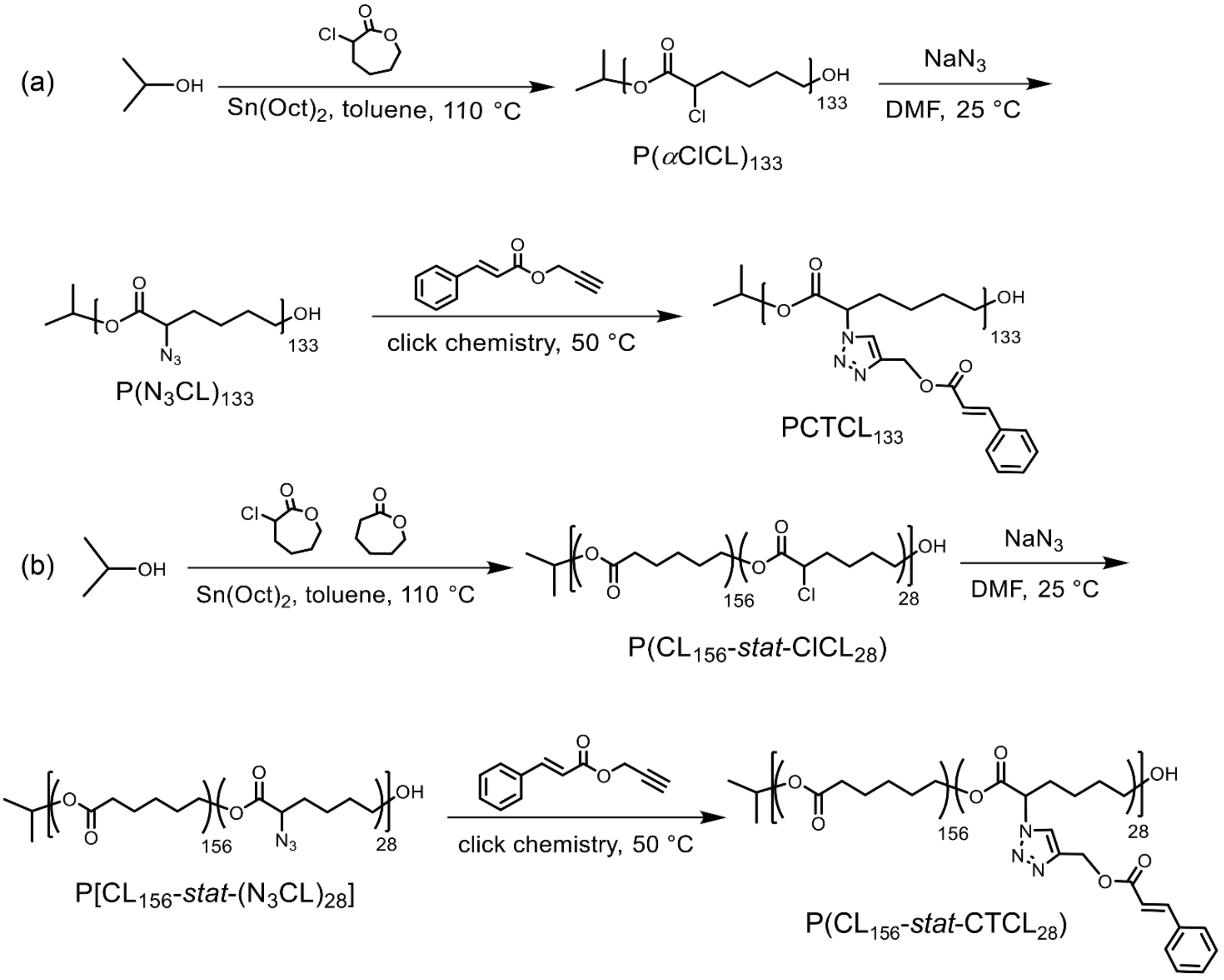
The parameters are as follows:

Geometry optimization: algorithm: smart; quality: fine; convergence tolerance: energy: 1.0 × 10^{-4} kcal·mol^{-1}, force: 0.005 kcal·mol^{-1}·Å^{-1}, displacement: 5.0 × 10^{-4} Å; maximum iterations: 500.

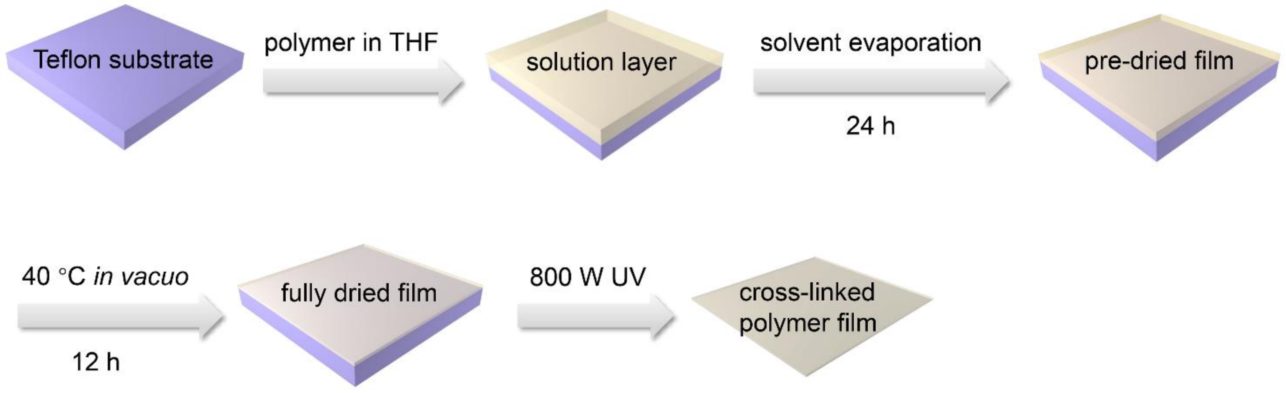
Dynamics: temperature: 298.00 K; ensemble: *NVT* (or *NPT*); timestep:1.00 fs; duration:50 ps. For successive dynamics simulations, the trajectory is appended to the former one. The pressure used for *NPT* simulations is 0.1 GPa and 101.3 kPa, respectively.

Mechanical properties: method: constant strain; number of steps for each strain: 4; maximum strain amplitude: 0.003. The mechanical property data were obtained after optimization with the same parameters of previously mentioned geometry optimization.

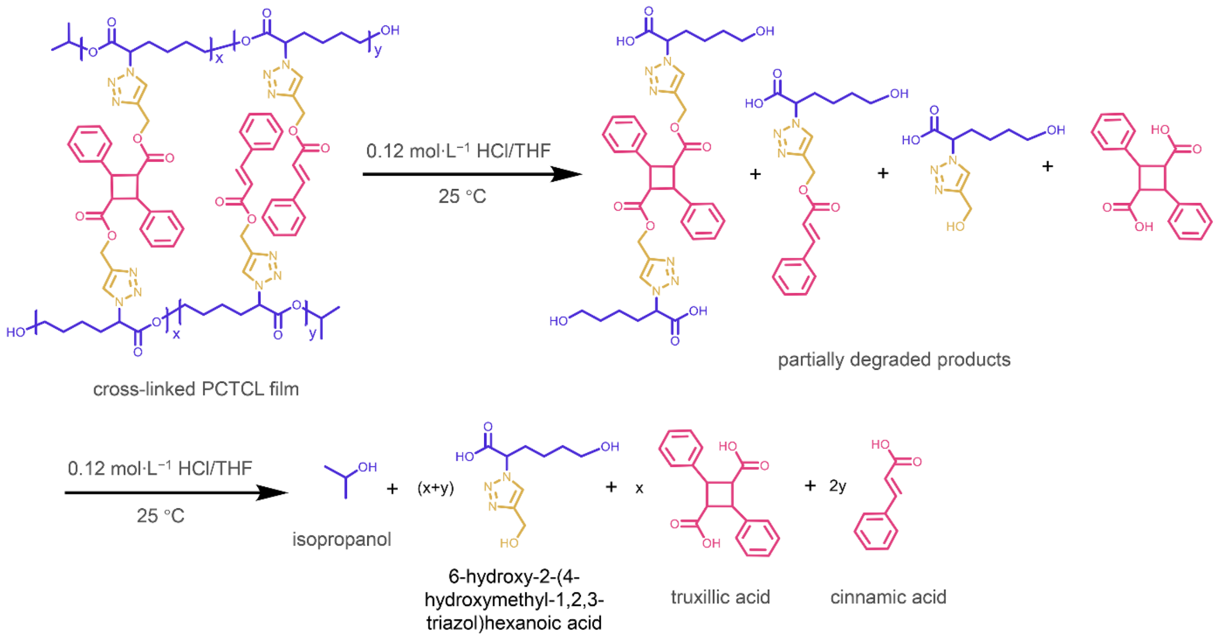
4 Supplementary Schemes



Scheme S1 Synthetic routes for (a) PCTCL$_{133}$ and (b) P(CL$_{156}$-*stat*-CTCL$_{28}$).



Scheme S2 Illustration for the preparation of cross-linked polymer films.



Scheme S3 Schematic illustration for completely degraded PCTCL film with a random cross-linking density D, where $D = \frac{x}{x+y}$.

5 Supplementary Figures

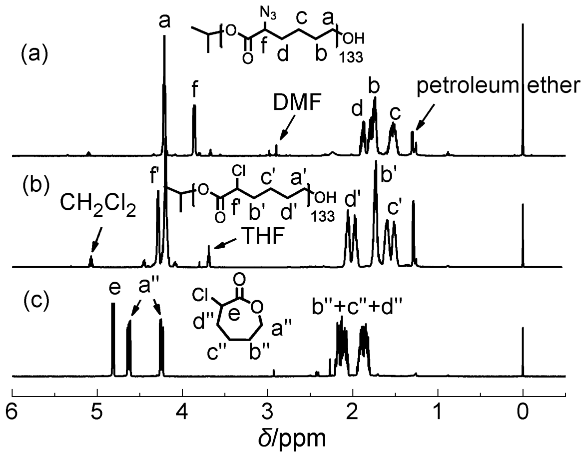


Fig. S1 ^{1}H NMR spectra of (a) $P(N_3CL)_{133}$, (b) $P(\alpha ClCL)_{133}$ and (c) αClCL in $CDCl_3$.

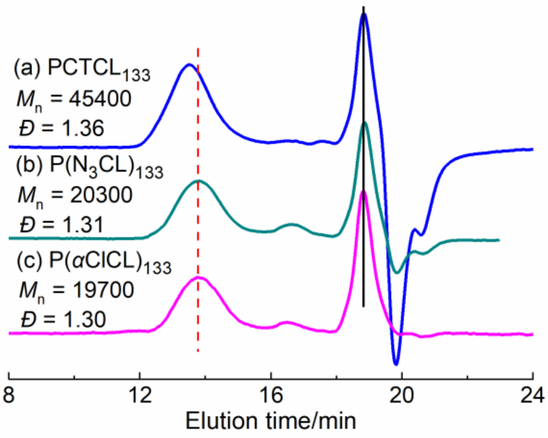


Fig. S2 THF SEC curves of (a) $PCTCL_{133}$, (b) $P(N_3CL)_{133}$ and (c) $P(\alpha ClCL)_{133}$.

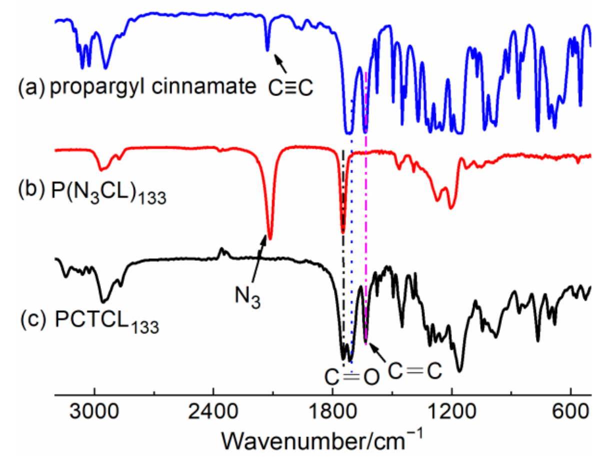


Fig. S3 FT-IR spectra of (c) PCTCL$_{133}$ and (a and b) its precursors.

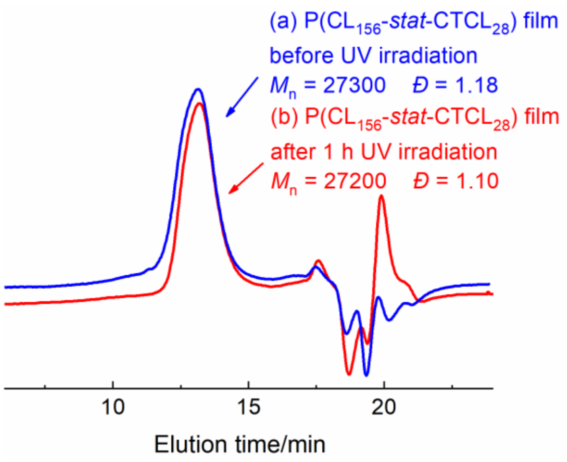


Fig. S4 THF SEC curves of the P(CL$_{156}$-*stat*-CTCL$_{28}$) film (a) before and (b) after UV irradiation.

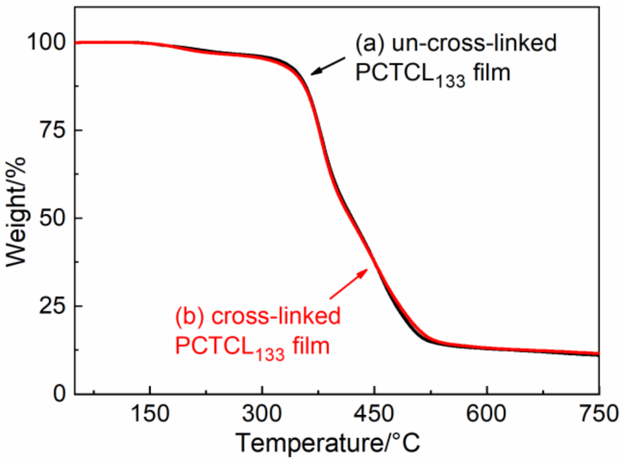


Fig. S5 TGA curves of (a) un-cross-linked PCTCL$_{133}$ film and (b) cross-linked PCTCL$_{133}$ film after 1 h UV irradiation. The curves were measured at a heating rate of 20 °C·min^{-1} under nitrogen atmosphere.

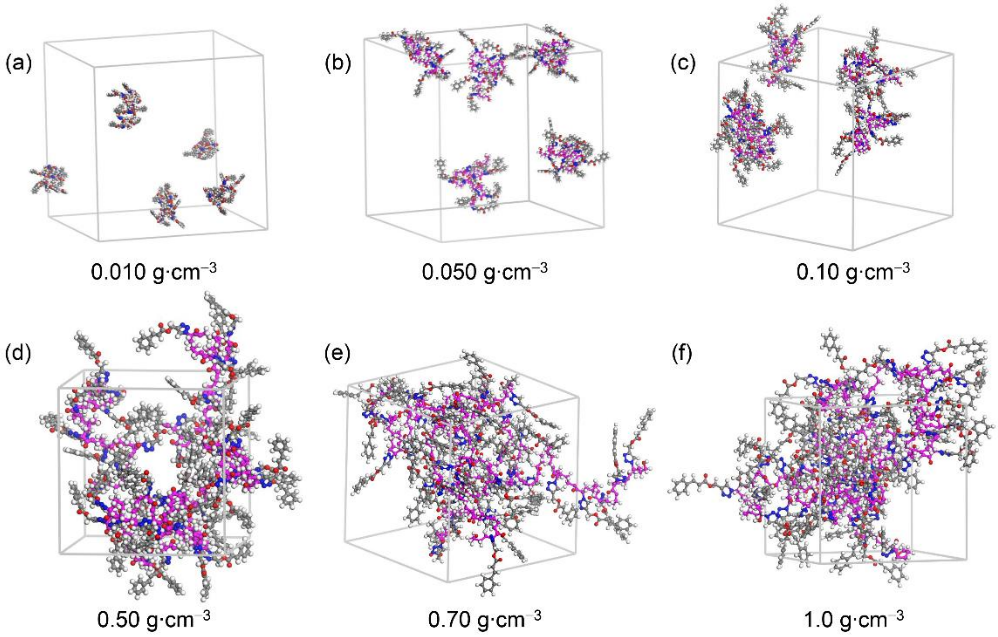


Fig. S6 Amorphous cells with different initial densities of polymer. Each cell consists of 5 PCTCL$_{10}$ chains, displayed in Default style. Beads with different colors represent different atoms: grey for carbon, white for hydrogen, blue for nitrogen and red for oxygen. The purple chains represent the backbones of PCTCL. The greyish cubic frame represents the repeating unit of each cell. As the density increases, polymers become more entangled with each other.

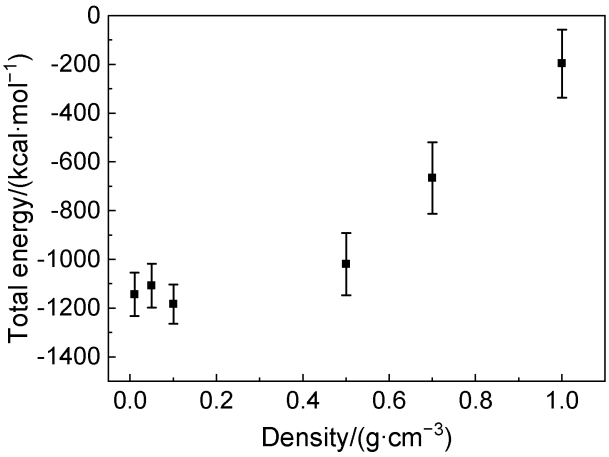


Fig. S7 Total energy data of the amorphous cells with different densities.

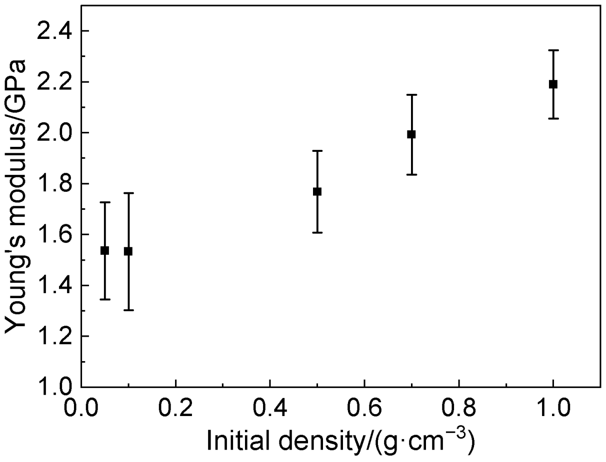


Fig. S8 Young's moduli of the model films originated from cells with different initial densities.

References

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