Supplementary Information (SI) for Polymer Chemistry.

Tunable Adhesion Properties of Hydrolytically Degradable Aliphatic Polyester Triblock/Diblock Copolymer Blends

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Materials

1,4-benzenedimethanol (BDM) was purchased from Sigma-Aldrich, recrystallized in toluene, and sublimed overnight at 100 °C under reduced pressure before storing under nitrogen in the glovebox. γ-Methyl-ε-caprolactone (γMCL) was purchased from Renewable Solutions, LLC and purified through fractional distillation at 70-100 °C under dynamic vacuum around 100 mTorr. *L*-lactide was provided by NatureWorks, LLC and recrystallized from anhydrous ethyl acetate (3 times) and anhydrous toluene (3 times) under an argon atmosphere and filtered in open air. After recrystallization, the *L*-lactide was dried for 24 hours at 80 °C under vacuum and was stored under a dry nitrogen atmosphere in a glovebox. Tin (II) 2-ethylhexanoate ($Sn(Oct)_2$) was purchased from Sigma-Aldrich and purified through three fractional distillations under dynamic vacuum, 145-170 °C with fractions cooled in a suspension of dry ice and isopropyl alcohol. The products were dried overnight under vacuum, purged with argon, and stored under nitrogen in the glovebox. Deuterium-chloroform ($CDCl_3$) was purchased from Cambridge Isotope Laboratories. Anhydrous toluene was obtained from a JC Meyer solvent drying system and stored over 4-Å molecular sieves under argon before using. The rosin ester tackifier (Sylvalite 2E 80HP) was provided by Kraton Chemical. All other chemicals were purchased from Sigma-Aldrich and used without further purification unless noted.

Synthesis of poly(*L*-lactide)-*block*-poly(γ-methyl-ε-caprolactone) (ML) dibolck copolymers, poly(*L*-lactide)-*block*-poly(γ-methyl-ε-caprolactone)-*block*-poly(*L*-lactide) (LML) triblock copolymers, and alkyne-terminated ML diblock copolymers

To synthesize alkyne-PγMCL macroinitiator, γMCL (10 g, 78 mmol), 3-butyn-1-ol (21.8 mg, 0.312 mmol) and $Sn(Oct)_2$ (32 mg, 0.078 mmol) were added into a pressure vessel equipped with a Teflon-coated magnetic stir bar under nitrogen atmosphere in the glove box. The vessel was sealed, taken out of the glove box, and placed in an oil bath preheated to 130 °C. After 90 minutes, the vessel was cooled in an ice bath to stop the reaction and dilute with chloroform. The solution was then precipitated into cold methanol (3 times) and hexanes (3 times) before drying in vacuum oven at room temperature for 48 hours.

To synthesize alkyne-ML triblock copolymers, alkyne-PγMCL (9g, 0.271 mmol) was dissolved in anhydrous toluene (41.6 ml) in the glove box under nitrogen atmosphere for 48 hours to achieve homogenous solution. *L*-lactide (3 g, 20.8 mmol) and $Sn(Oct)_2$ (9.4 mg, 0.0208 mmol) were then added into the solution in a pressure vessel equipped with a Teflon-coated magnetic stir bar. The vessel was sealed, taken out of the glove box, and placed in an oil bath preheated to 130 °C. After 90 min, the vessel was cooled in an ice bath to stop the reaction and dilute with chloroform. The solution was then precipitated into cold methanol (3 times) and hexanes (3 times) before drying in vacuum oven at room temperature for 48 h.

To synthesize ML diblock copolymers without alkyne termination, but similar composition and molar mass, same process and parameters were used except replacing 3-butyn-1-ol with benzyl alcohol (33.7 mg, 0.312 mmol).

To synthesize LML triblock copolymers without alkyne termination, but similar compositions and arm length, same process and parameters were used except replacing 3-butyn-1-ol with BDM (21.5 mg, 0.155 mol).

Synthesis of *α*,*α'*-diazido-*p*-xylene bifunctional linker

α,*α'*-dibromo-*p*-xylene (2.64 g, 10 mmol) was dissolved in 20 ml of dimethylformamide (DMF) before the addition of sodium azide (1.3 g, 20 mmol). The solution was stirred for 24 hours at room temperature. The product was extracted by diethyl ether, washed with brine (2 times), and dried with sodium sulfate. The solvent was then evaporated by rotary evaporation, leaving yellowish solid product. The product was dried in vacuum oven at room for 12 h before storing in fridge.

Synthesis of LML/ML blends with different LML contents by copper-catalyzed alkyne-azido cycloaddition reaction

Alkyne-ML diblock copolymers were dissolved in THF with a concentration of 0.1 g/ml under stirring. *α*,*α'*-diazido-*p*-xylene, copper (I) bromide (CuBr) and N,N,N,N,N-pentamethyldiethylenetriamine (PMDETA) were then added into the THF solution in a round-bottom flask. The round-bottom flask were then purged with argon and covered with alumina foil to avoid light exposure.

The molar ratio of alkyne termination on alkyne-ML diblock copolymer to azido group on *α*,*α'*-diazido-*p*-xylene, CuBr, and PMDETA is 1: 0.4 :5 : 10 for LML/ML blends with 25 wt% of LML, 1: 0.75: 5: 10 for LML/ML blends with 50 wt% of LML, and 1: 1.1: 5: 10 for LML/ML blends with 75 wt% of LML.

After continuous stirring for 24 h, the solution was concentrated to half volume by rotary evaporation, followed by precipitation in cold methanol. The solid product was dissolved in chloroform before passing through a neutral alumina column to remove CuBr and PMDATE. The solution was then precipitated into cold methanol again to obtain white, solid product of LML/ML blends.

Synthesis of LML/ML blends with 50 wt% of LML via sequential ring-opening transesterification polymerizations with the presence of both benzyl alcohol and BDM

To synthesize PγMCL macroinitiator, γMCL (10 g, 78 mmol), benzyl alcohol (14.5 mg, 0.208 mmol), BDM (14.4 mg, 0.104 mmol) and $Sn(Oct)_2$ (32 mg, 0.078 mmol) were added into a pressure vessel equipped with a Teflon-coated magnetic stir bar under nitrogen atmosphere in the glove box. The vessel was sealed, taken out of the glove box, and placed in an oil bath preheated to 130 °C. After 90 minutes, the vessel was cooled in an ice bath to stop the reaction and dilute with chloroform. The solution was then precipitated into cold methanol (3 times) and hexanes (3 times) before drying in vacuum oven at room temperature for 48 h.

To synthesize LML/ML blends, PγMCL (9g) was dissolved in anhydrous toluene (41.6 ml) in the glove box under nitrogen atmosphere for 48 hours to achieve homogenous solution. *L*-lactide (3 g, 20.8 mmol) and $Sn(Oct)_2$ (9.4 mg, 0.0208 mmol) were then added into the solution in a pressure vessel equipped with a Teflon-coated magnetic stir bar. The vessel was sealed, taken out of the glove box, and placed in an oil bath preheated to 130 °C. After 90 min, the vessel was cooled in an ice bath to stop the reaction and dilute with chloroform. The solution was then precipitated into cold methanol (3 times) and hexanes (3 times) before drying in vacuum oven at room temperature for 48 hours.

Thin film preparation of LML/ML blends for characterizations

LML/ML blends were dissolved in chloroform overnight to yield a 20 wt% homogeneous solution, followed by casting onto a fluorinated ethylene propylene (FEP) substrate (100 μm, McMaster-Carr) using a wire wound rod. The films were then dried flow for 48 h at room temperature and detached from the FEP substrate for characterizations.

Pressure-sensitive adhesive (PSA) preparation

LML/ML blends with 20 wt% tackifier were dissolved in chloroform overnight to yield a 20 wt% homogeneous solution, followed by casting onto a poly(ethylene terephthalate) (PET) substrate (40 μm, ChemInstruments) using a wire wound rod. The PSAs were then dried under continuous nitrogen flow at room temperature for 48 hours. The thickness of the dried film was roughly 80 μm.

For the two-step annealing, the PSAs were first put into an oven preheated to 170 °C for 1 hour under nitrogen atmosphere, followed by rapid quenching (approximately 35 °C/min) to room temperature on a cold metal substrate. Subsequently, the PSAs were put into an oven preheated to 100 °C for 5 minutes under nitrogen atmosphere, followed by rapid quenching (approximately 35 °C/min) to room temperature on a cold metal substrate.

Adhesive testing

Standard test methods used for peel adhesion and shear strength were PSTC:101 and PSTC:107, respectively. The polished stainless steel panels (PSTC 304 BRT, 18 Gauge) were used as the adherent for adhesion testing.

180° peel test: a 1 cm wide strip of the PSA coated-PET film was adhered to a panel using a 2 kg rubber roller. The sample was tested by a Shimadzu ASG-X tensile tester at a peel rate of 305 mm min^{-1}. The peel strength was recorded as the plateau force. The test was performed at least three times and averaged across the samples except for the occasional clear outlier samples.

Shear resistance test: A PSA coated-PET film was adhered to a stainless steel panel forming a contact area of 2.54 cm × 2.54 cm, and pressed by a rubber roller. A 1000 g weight was applied to the sample, and the time to failure (weight drop) was recorded, and averaged across at three samples.

Loop tack adhesion test: A 1 cm wide strip of the PSA coated–PET film was made into a teardrop shaped loop and mounted to the upper grip of the tensile tester while a stainless-steel panel was mounted on the lower grip. Then the loop was gently lowered forming a contact area of 1 cm × 1.5–2 cm. The tack strength was monitored while the upper grip was lifted at a rate of 305 mm min−1. The tack strength was recorded as the maximum measured force divided by the area. The test was performed at least three times and averaged across all samples except for the occasional clear outlier result.

Hydrolytic degradation test

PSA coated-PET film was cut into 1 cm × 1 cm square before dispersing in a vial of either ~20 ml 1 M NaOH aqueous solution. The vials were then put into an oven at 45 °C. 50 µL aliquots at various time points were taken out from the vials, diluted with 9950 µL deionized water before total organic carbon (TOC) measurement using a Shimadzu TOC-L analyzer. Controlled experiments of PET films were also conducted under same conditions.

Controlled experiments of PET films and tackifier powders under exactly same conditions and measurement can be found in previous work.[1]

Characterization

^{1}H-NMR and ^{13}C-NMR spectra were obtained from 400 MHz Bruker Avance III HD with SampleXpress.

Size exclusion chromatography (SEC) was performed with tetrahydrofuran (THF) as mobile phase (25 °C, 1 mL min^{-1}) on an Agilent Infinity 1260 HPLC system equipped with Waters Styragel HR columns, a Wyatt HELEOS-II multiangle laser light scattering (MALS) detector, and a Wyatt Optilab T-rEX S7 differential refractive index detector.

Small-angle X-ray scattering (SAXS) was acquired from 15-minute exposures in the Characterization Facility, University of Minnesota, using a Xenocs instrument (Ganesha). Thin film samples were prepared by solvent casting from chloroform (20 wt% solution) into 400 µm films using a wire wound rod on fluorinated ethylene propylene (FEP) substrate (100 µm, McMaster-Carr). The films were dried under nitrogen flow for 48 h at room temperature (no solvent residue confirmed by ^{1}H NMR) and detached from the FEP substrate before mounting up on Kapton tape and exposure at room temperature.

Thermal properties were investigated via differential scanning calorimetry measurements under nitrogen flow with a TA Instruments Discovery Series differential scanning calorimeter and a refrigerated cooling system.

Linear viscoelastic properties were probed via small amplitude oscillatory shear (SAOS) experiments with a TA ARES G2 rheometer and 8 mm parallel-plate fixture. Samples were processed after specific history before molding on the rheometer at 80 °C. All experiments were carried out in the linear viscoelastic region determined by dynamic strain sweep at -20 °C and a frequency of 1 rad s^{-1}. Frequency sweeps were performed at 1 % strain and temperatures from –20 to 80 °C.

Tensile testing was performed Shimadzu AGS-X 500N tensile tester with the accompanying Trapezium software. A constant extension rate of 305 mm min^{-1} was used for all samples.

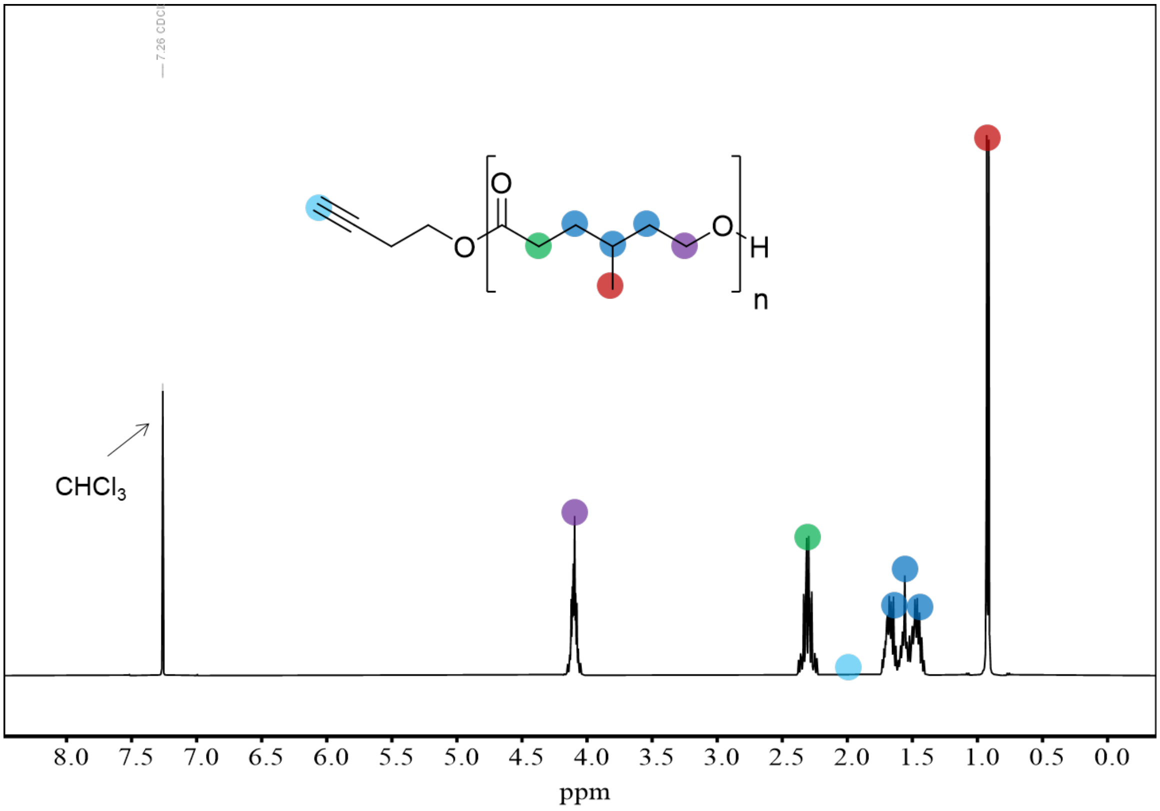

Figure S1. ^{1}H-NMR spectra of alkyne-terminated PγMCL(31.1). CDCl$_3$, 400 MHz, 64 scans, d$_1$ = 10 s.

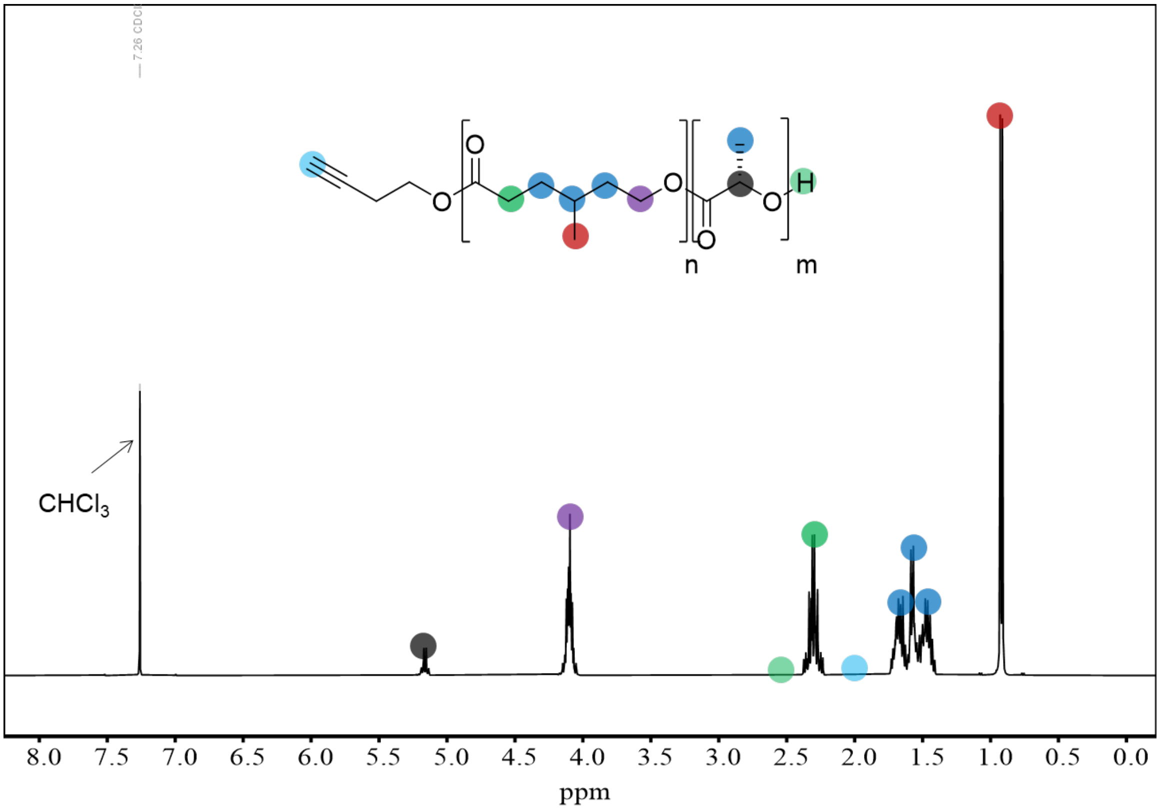

Figure S2. ^{1}H-NMR spectra of alkyne-ML(38.8, 0.26). $CDCl_3$, 400 MHz, 64 scans, d_1 = 10 s.

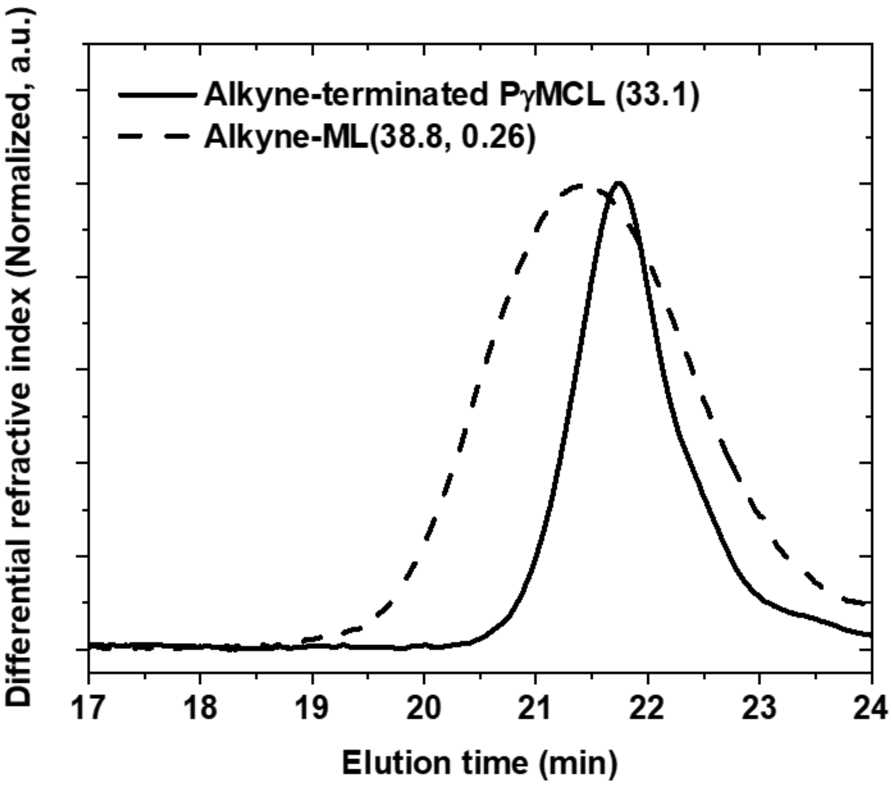

Figure S3. Tetrahydrofuran (THF) SEC traces of alkyne-terminated P*γ*MCL(33.1) and alkyne-ML(38.8, 0.26).

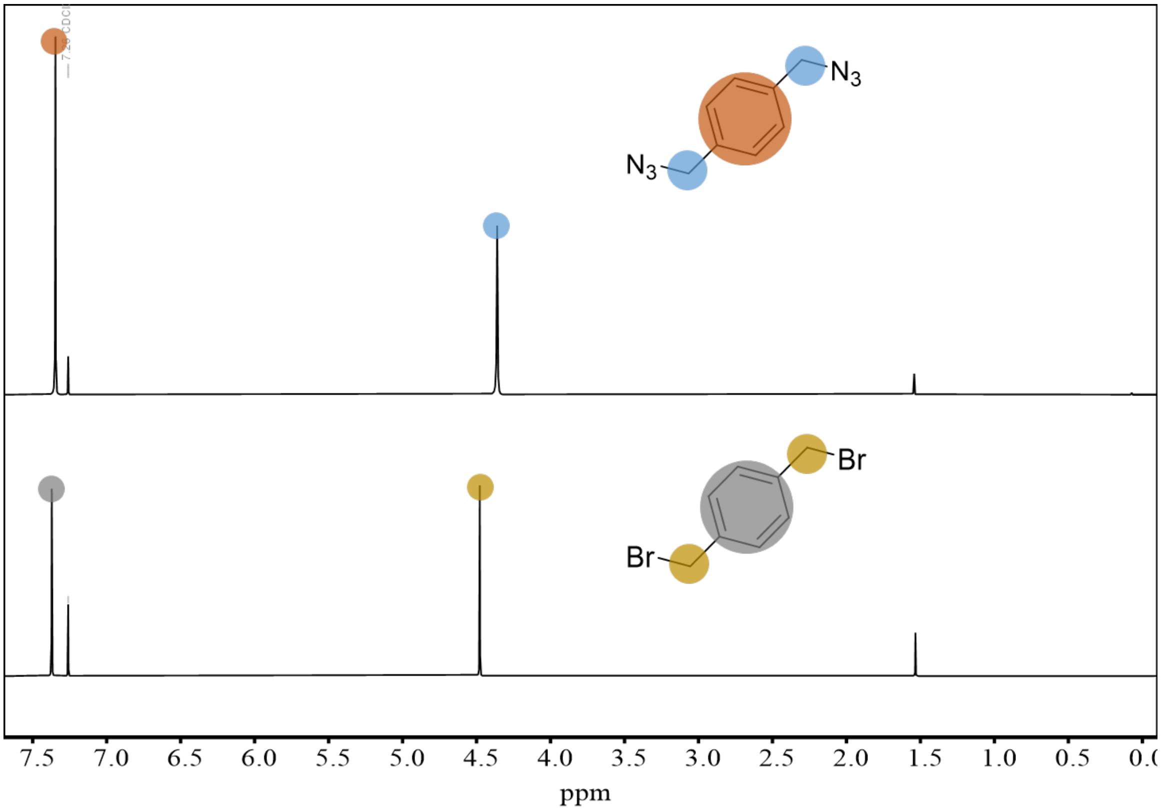

Figure S4. ^{1}H-NMR spectra of *α*,*α′*-dibromo-*p*-xylene (bottom) and as-prepared *α*,*α′*-diazido-*p*-xylene linker (top). $CDCl_3$, 400 MHz, 16 scans, d_1 = 1 s.

Table S1. Molecular characteristics of the ML and LML block copolymers without alkyne termination.

Sample ID ($M_{n,total}$, f_{PLLA})	$M_{n,\ P\gamma MCL}$ (kg mol^{-1})^{a}	$M_{n,\ PLLA}$ (kg mol^{-1})^{a}	$M_{n,total}$ (kg mol^{-1})^{a}	$M_{n,SEC,MALLS}$ (kg mol^{-1})^{b}	$Đ^{c}$	$f_{PLLA}{}^{d}$
LML(74.0, 0.25)	63.3	10.7	74.0	120.9	1.25	0.25
ML(37.5, 0.22)	32.1	5.4	37.5	29.7	1.55	0.22

[a] Determined using proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) end-group analysis with deuterated $CHCl_3$ as solvent. [b] Determined using THF-SEC with multi-angle laser light scattering (MALLS) detector. [c] Determined using THF-SEC with differential refractive index (RI) detector. [d] Total PLLA volume fraction calculated from block M_n values using $\rho_{P\gamma MCL} = 1.037$ g cm^{-3} and $\rho_{PLLA} = 1.25$ g cm^{-3}.

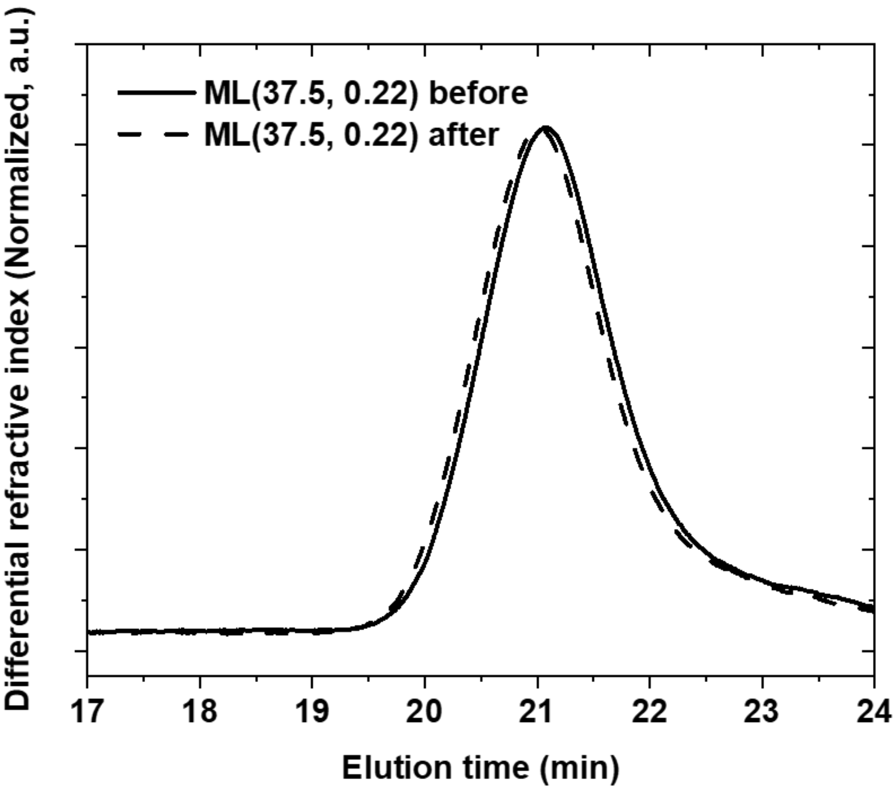

Figure S5. Tetrahydrofuran (THF) SEC traces of ML(37.5,0.22) without alkyne termination before and after copper-catalyzed alkyne-azido cycloaddition reaction. To assess potential side reaction from nitrene insertion, a control sample of ML(37.5, 0.22) (**Table S1**, where 37.5 is the total molar mass of ML and 0.22 is f_{PLLA}) with similar molar mass and composition was prepared via two-step ROTEPs without alkyne-functionalized initiator, but benzyl alcohol as initiator, followed by copper-catalyzed alkyne-azido cycloaddition reaction with *α*,*α'*-diazido-*p*-xylene linker under same conditions. The SEC traces of the ML(37.5, 0.22) displayed almost identical peak shapes and elution times, indicating that nitrene insertion reaction is very unlikely under these conditions.

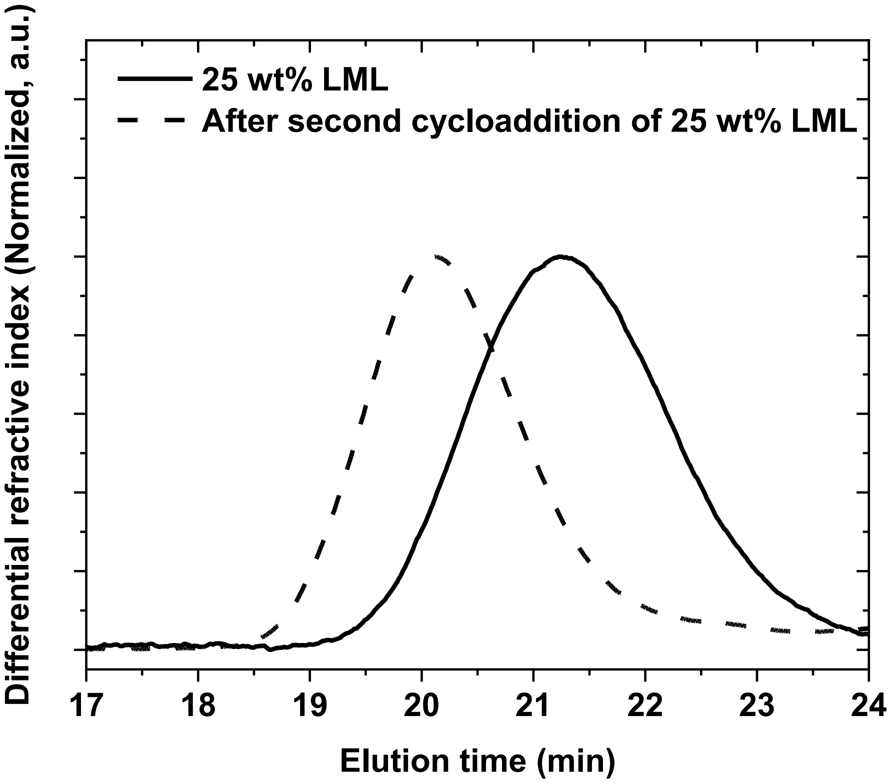

Figure S6. THF SEC traces of 25 wt% LML blends before and after second copper-catalyzed alkyne-azido cycloaddition reaction.

Table S2. Molar mass and dispersity of 25 wt% LML blend before and after second copper-catalyzed alkyne-azido cycloaddition reaction.

Sample ID ($M_{n,total}$, f_{PLLA})	$M_{n,SEC,MALLS}$ (kg mol^{-1})[a]	$Đ$[b]
25 wt% LML	45.5	1.41
After second cycloaddition	77.8	1.33

[a]Determined using THF-SEC with multi-angle laser light scattering (MALLS) detector. [b]Determined using THF-SEC with differential refractive index (RI) detector.

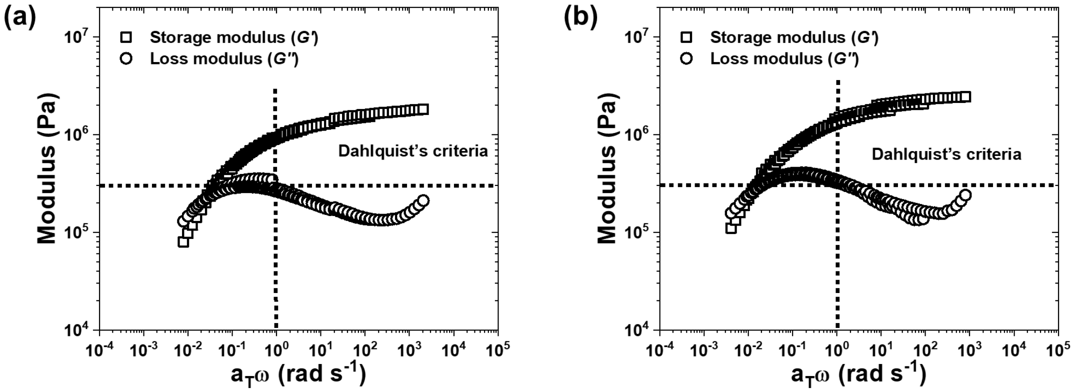

Figure S7. Master curves for the storage modulus (G') and loss modulus (G'') of (a) 25 wt% LML blend and (b) 50 wt% LML blend after solvent casting. The Dahlquist criterion (G< 0.3 MPa at 1 rad s^{-1}) is marked by dashed lines.

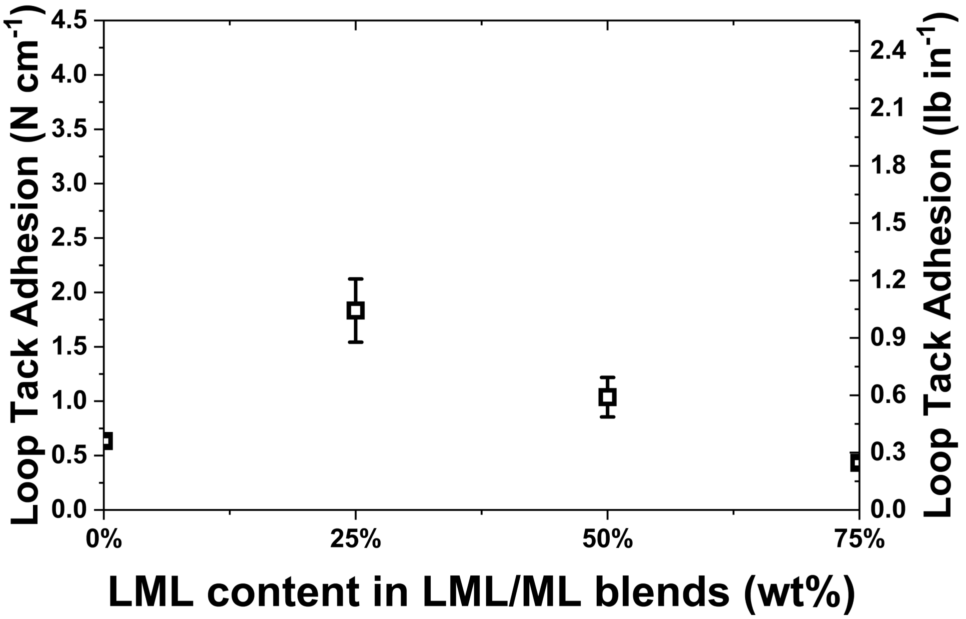

Figure S8. Loop tack adhesion results tested with stainless steel substrates for alkyne-ML(38.8, 0.26) and LML/ML blends after solvent casting with 20 wt% tackifier. The tests were performed at a rate of 305 mm min^{-1}. The loop tack adhesion strength of the tackified PSAs were: 0.63 ± 0.42 N cm^{-1} (alkyne-ML(38.8, 0.26)), 1.83 ± 0.29 N cm^{-1} (25 wt% LML), 1.04 ± 0.18 N cm^{-1} (50 wt% LML), and 0.43 ± 0.04 N cm^{-1} (75 wt% LML).

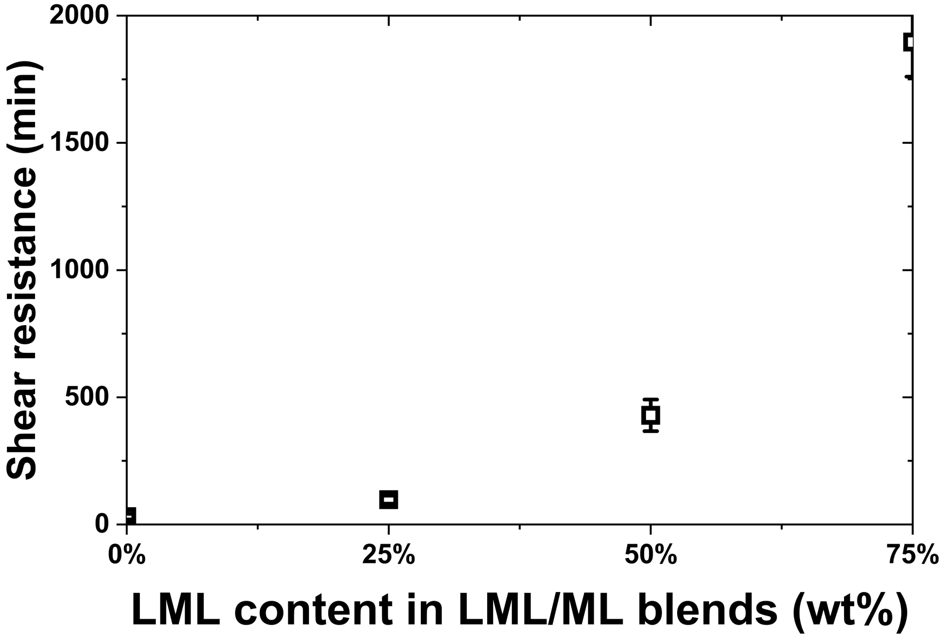

Figure S9. Shear resistance properties on stainless steel substrates of alkyne-ML(38.8, 0.26) and LML/ML blends after solvent casting with additional 20 wt% tackifier, first annealing at 170 °C for 60 minutes, second annealing at 100 °C for 5 minutes, and rapid cooping to room temperature.

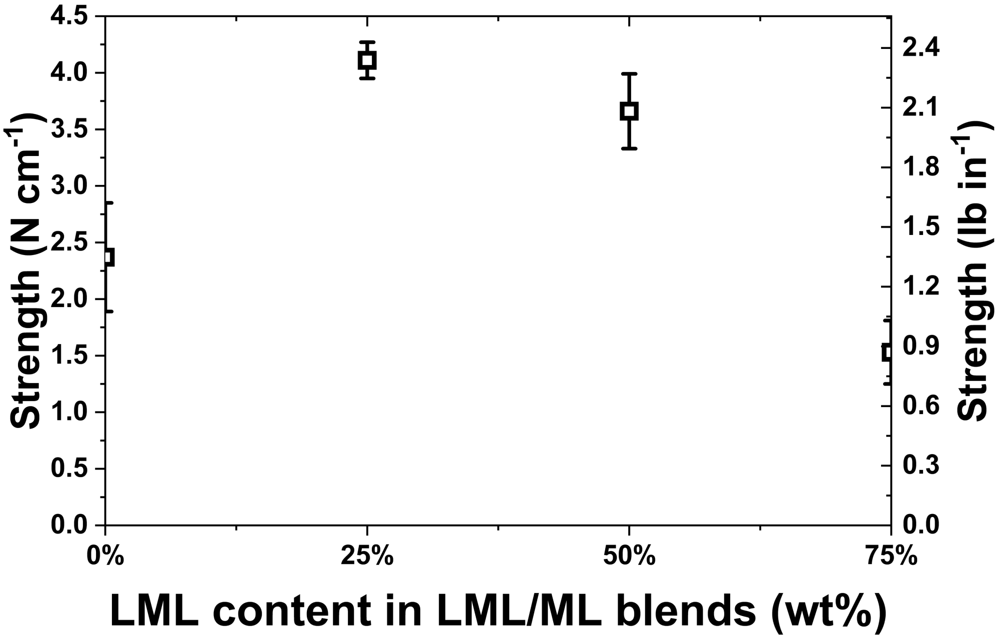

Figure S10. 180° peel adhesion properties on stainless steel substrates of alkyne-ML(38.8, 0.26) and LML/ML blends after solvent casting with additional 20 wt% tackifier, first annealing at 170 °C for 60 minutes, second annealing at 100 °C for 5 minutes, and rapid cooping to room temperature. All of the 180° peel adhesion tests were performed at the rate of 305 mm min^{-1}.

Table S3. Adhesion properties of PSA from alkyne-ML(38.8, 0.26) and LML/ML blends after solvent casting with additional 20 wt% tackifier, first annealing at 170 °C for 60 minutes, second annealing at 100 °C for 5 minutes, and rapid cooping to room temperature.

Sample ID	Peel strength (N cm^{-1})	Peel adhesion failure mode	Shear (min)
Alkyne-ML(38.8, 0.26)	2.37±0.48	Cohesive failure	31±11
25 wt% LML	4.11±0.16	Cohesive failure	98±16
50 wt% LML	3.66±0.33	Adhesive failure	429±62
75 wt% LML	1.53±0.28	Adhesive failure	1896±136

Table S4. Molecular characteristics of the LML/ML blends synthesized in one set of sequential ring-opening polymerizations.

Sample ID	$M_{n,\, P\gamma MCL,SEC,MALLS}$ (kg mol^{-1})^{a}	$M_{n,SEC,MALLS}$ (kg mol^{-1})^{a}	$Đ^{b}$	$f_{PLA}{}^{c}$
Simultaneous polymerization	40.8	43.8	1.47	0.35

[a]Determined using THF-SEC with multi-angle laser light scattering (MALLS) detector. [b]Determined using THF-SEC with differential refractive index (RI) detector. [c]Total PLA volume fraction calculated from proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) with deuterated $CHCl_3$ as solvent using $\rho_{P\gamma MCL}$ = 1.037 g cm^{-3} and ρ_{PLLA} =1.25 g cm^{-3}.

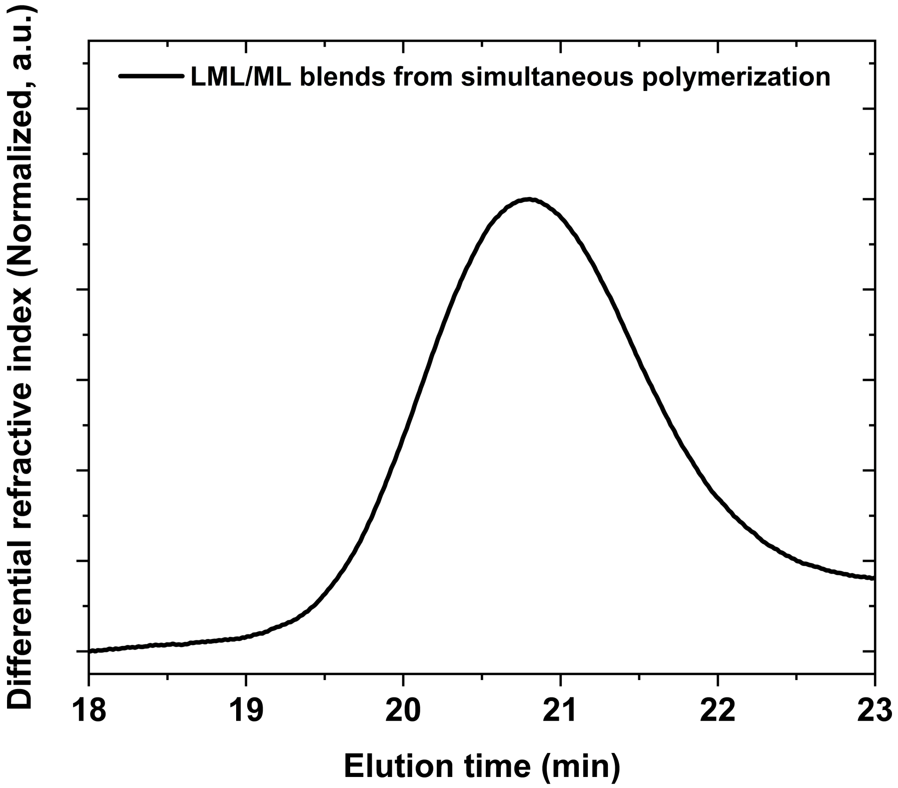

Figure S11. Tetrahydrofuran (THF) SEC trace of the LML/ML blends synthesized in one set of sequential ring-opening polymerizations.

Table S5. Peel adhesion properties of tackified PSAs (20 wt% tackifier) from LML/ML blends with 50 wt% LML prepared from different routes after solvent casting.

Synthetic strategy	Peel strength (N cm^{-1})	Peel adhesion failure mode
Azide-alkyne coupling	1.98±0.37	Cohesive/adhesive failure
Post-synthesis blending	1.65±0.25	Adhesive failure
Simultaneous polymerization	1.21±0.52	Adhesive failure

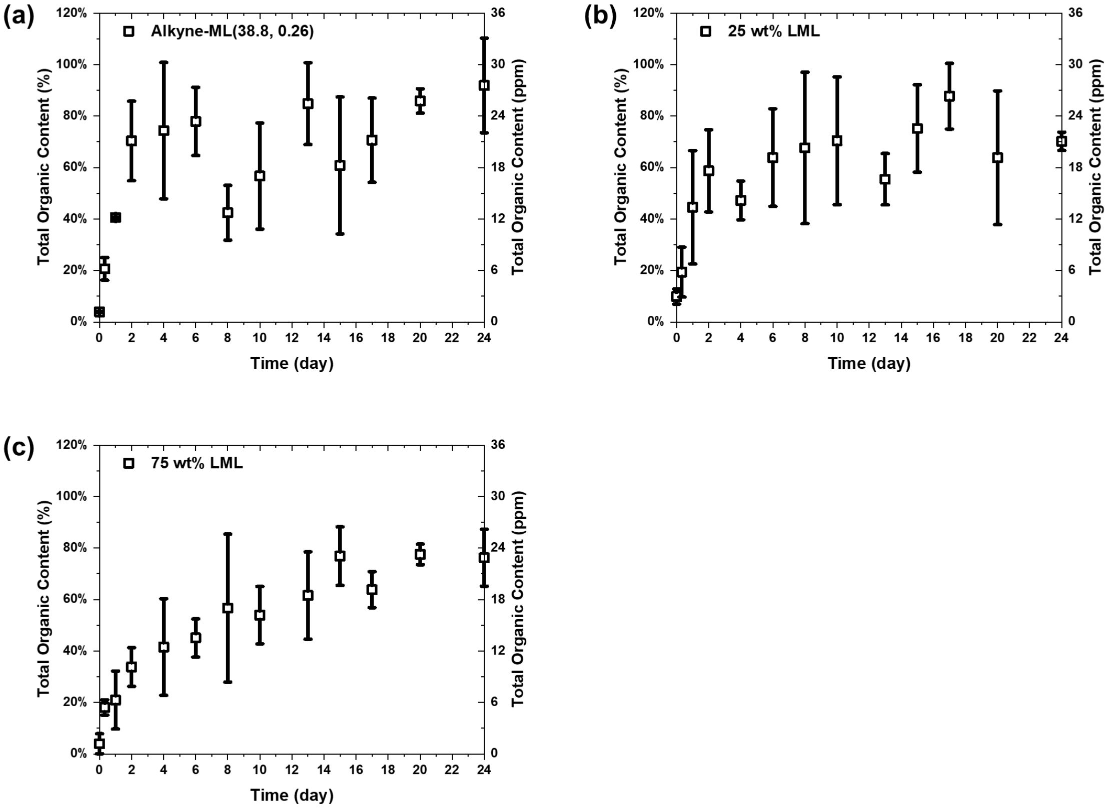

Figure S12. Hydrolytic degradation studies in 1 M NaOH aqueous solution at 45 °C of tackified PSA (20 wt% tackifier) from (a) alkyne-ML(38.8, 0.26), (b) LML/ML blends with 25 wt% LML and (c) LML/ML blends with 75 wt% LML after solvent casting. The total organic carbon (TOC) content is the ratio of measured organic carbon in the aqueous solutions to the theoretical carbon content of the blends. The data points and error bars represent median and range for triplicate experiments, respectively.

References

1. Liang, S.; Krajovic, D. M.; Hoehn, B. D.; Ellison, C. J.; Hillmyer, M. A., Engineering Aliphatic Polyester Block Copolymer Blends for Hydrolytically Degradable Pressure Sensitive Adhesives. *ACS Appl. Polym. Mater.* **2024,** *7* (3), 1411-1420.