

Supporting Information for Manuscript Entitled with
**Chemoselective and Controlled Ring-Opening
Copolymerization of Biorenewable α -Methylene- δ -
Valerolactone with ϵ -Caprolactone toward Functional
Copolyesters**

Yalei Liu,^a Xinhui Kou,^b Chen Xu,^a Wei Zhou,^a Hongshu Zhang,^a Fusheng

*Liu,^{*a} Yong Shen^{*a} and Zhibo Li^{*, a, c}*

^a State Key Laboratory Base of Eco-Chemical Engineering; College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, China.

^b Analyses and testing center, Qingdao University of Science and Technology, Qingdao 266042, China.

^c Key Laboratory of Biobased Polymer Materials, Shandong Provincial Education Department; Qingdao University of Science and Technology, Qingdao 266042, China.

Corresponding authors: E-mail: liufusheng63@sina.com

E-mail: shenyong@qust.edu.cn

E-mail: zbli@qust.edu.cn

Experimental Section

Materials

Tetrahydrofuran (THF) was refluxed with sodium for 4 hours and then distilled and stored in a glove box. Toluene (TOL) was refluxed with sodium for 4 hours and then distilled and stored in a glove box. *N, N*-dimethylformamide (DMF) was refluxed

with CaH₂ for 4 hours and then distilled under reduced pressure. Potassium methoxide (KOME, 95%) was obtained from Sigma-Aldrich Chemical Co. 1-*Tert*-butyl-2, 2, 4, 4, 4-pentakis(dimethylamino)-2λ⁵, 4λ⁵-catenadi-(phosphazene) (*t*Bu-P₂) was purchased from Sigma-Aldrich Chemical Co. Benzyl alcohol (BnOH, 99%) was obtained from J&K Scientific. Delta-valerolactone (δ-VL, 95%) and epsilon-caprolactone (CL, 95%) obtained from Alfa Aesar Co. were stirred with CaH₂ for 48 hours, then distilled under reduced pressure. Ethyl formate (98%) and paraformaldehyde (POM, 95%) were obtained from Aladdin Reagent Co. Sodium hydride (NaH, 60% dispersion in mineral oil) was obtained from Energy Chemical Co. Anhydrous potassium carbonate (K₂CO₃, 99%), magnesium sulphate (MgSO₄, 98%) and sodium chloride (NaCl, 99.8%) were obtained from Sinopharm Chemical Reagent Co. Benzyl mercaptan was obtained from Acros Organics. β-Mercaptoethanol was obtained from Shanghai Macklin Biochemical Technology Co. The cyclic trimeric phosphazene base (CTPB) was synthesized according to the reported procedure¹. All commercially obtained reagents were used as received without further purification unless otherwise noted.

Instruments

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVNEO400ASCEND FT-NMR spectrometer at 400 MHz for ¹H NMR and 100 MHz for ¹³C NMR. Chemical shifts were reported in δ (ppm) relative to the residual deuterated solvent peak. Size exclusion chromatography (SEC) experiments were performed on an Agilent HPLC system equipped with a model 1260 Hip degasser, a model 1260 Iso pump and a model 1260 differential refractometer detector with using THF as mobile phase at a flow rate of 1.0 mL/min at 40 °C. One PLgel 5 μm guard column and three Mz-Gel SD_{plus} columns (10³ Å, 10⁴ Å, and 10⁵ Å, linear range of MW = 1000 – 2*10⁶ Da) were connected in series. Quantitative ¹³C NMR analyses of polymer microstructure were recorded with inverse-gated decoupled pulse programs. Sweep width was set to 20000 Hz on a 400 MHz spectrometer, the number of scans was 1024, the total number of data points collected was 18000, and relaxation delays (D1) were limited to 10 s. The molecular weights and dispersities were calculated

using 10 polystyrene standards with narrow dispersities as references. The sample concentration used for SEC analyses was 5-10 mg/mL. Differential scanning calorimetry (DSC) measurements were performed on a TA instrument DSC 25. Temperature was calibrated with an indium standard. Measurements were performed under N₂ atmosphere with a flow rate of 50 mL/min. Each sample with a mass of 5-10 mg was used for the measurement. The typical procedures for the measurements were as follows: in the first heating scan, samples were heated from -80 to 150 °C at a heating rate of 10 °C/min and kept at 150 °C for 2 min to eliminate any thermal history. In the second heating scan, samples were cooled to -80 °C at 10 °C/min and then equilibrium at -80 °C for 2 min, and subsequently reheated to 150 °C at 10 °C/min. Thermogravimetric analysis (TGA) measurements were performed on a STA 800 thermogravimetric analyzer. The samples were heated from 40 to 600 °C at a heating rate of 10 °C/min under N₂ atmosphere with a flow rate of 40 mL/min.

Preparation of MVL

The monomer was prepared according to previously reported procedures.² The obtained monomer was stirred with CaH₂ for 48 hours, then distilled under reduced pressure and stored in a glove box.

Preparation of ureas

The ureas were prepared according to previously reported procedures.^{3, 4} The obtained ureas were dried under vacuum at 50 °C for at least 48 hours and then stored in a glove box.

General copolymerization procedure

All moisture-sensitive operations were conducted using standard Schlenk techniques or in a glovebox filled with high-purity nitrogen. A 25 mL flame-dried Schlenk tube was charged with predetermined amounts of benzyl alcohol (BnOH), 1-*tert*-butyl-2, 2, 4, 4, 4-penta(dimethylamino)-2Λ⁵, 4Λ⁵-di(phosphonium) (*t*Bu-P₂), urea and solvent in a glovebox. The Schlenk tube was sealed with a septum and removed out of the glovebox. A mixture of MVL and CL with a designed ratio was then injected into the

Schlenk tube via a syringe to start the copolymerization. After a period of time, a few drops of acetic acid were added to quench the polymerization. Two aliquots of the reaction mixture were withdrawn, and used for ^1H NMR and SEC measurement to determine the monomer conversion and molecular weight, respectively. The remaining reaction mixture was poured into excess cold methanol. The precipitate was washed with methanol three times and then dried under vacuum to obtain the product.

General procedure for the kinetic experiment

The polymerization was conducted at a feeding molar ratio of $[\text{MVL}]_0/[\text{CL}]_0/[t\text{Bu-P}_2]/[\text{U3}]/[\text{BnOH}] = 100/100/1/1.5/1$ followed the general polymerization procedure. Several parallel experiments were performed but quenched at certain time intervals by acetic acid solution in CHCl_3 . Two aliquots of solution were withdrawn and diluted using CDCl_3 . The MVL conversion was determined by ^1H NMR measurement. The molar mass M_n and dispersity D were determined by SEC.

General procedure for post-functionalization of P(MVL-*co*-CL)

A mixture of 86.4 mg P(MVL-*co*-CL) ($M_n = 26.1$ kDa), (5 equiv., 2 mmol) thiol (relative to the vinyl group), and (0.05 equiv., 0.02 mmol, 2.8 μL) triethylamine was dissolved in 0.4 mL dimethyl sulfoxide (DMSO). The reaction was conducted at 40 $^\circ\text{C}$ for 5 h. An aliquot of reaction mixture was withdrawn and used to determine the conversion by ^1H NMR measurement. The remaining mixture was poured into excess cold methanol (-20 $^\circ\text{C}$). The obtained precipitate was washed with cold methanol twice and then dried under vacuum at room temperature.

Table S1. Kinetic data of ROCP of MVL with CL obtained at $[MVL]_0/[CL]_0/[tBu-P_2]/[U3]/[I] = 100/100/1/1.5/1^a$

Run	Time (s)	Conv. (MVL%) ^b	Conv. (CL%) ^b	Conv. (overall, %) ^c	Incorp. (MVL mol%) ^b	$M_{n, SEC}$ (kDa) ^d	\bar{D} ^d
1	10	58.0	5.6	31.8	91.2	6.4	1.09
2	20	78.3	10.7	44.5	88.0	9.3	1.07
3	60	94.8	23.5	59.1	80.1	12.4	1.06
4	120	97.6	51.0	74.3	65.7	16.2	1.06
5	180	98.4	61.0	79.7	61.7	17.3	1.13
6	480	99.4	91.1	95.2	52.2	20.9	1.18

^a Conditions: 0.02 mmol BnOH was used. The copolymerizations were conducted at $[MVL]_0 = 4$ M at 0 °C in TOL. ^b Monomer conversions and MVL incorporations were determined by ¹H NMR.

^c The overall conversion was calculated from the feeding molar ratio and monomer conversion as $Conv.(overall) = (([MVL]_0/[I] * Conv.(MVL) + [CL]_0/[I] * Conv.(CL)) / ([CL]_0/[I] + [MVL]_0/[I]))$.

^d Determined by SEC in THF relative to PS standards.

Table S2. Results of ROCP of MVL with CL obtained at varied $[M]_0/[BnOH]$ ratios ^a

Run	$[MVL]_0/[CL]_0/[tBu-P_2]/[U3]/[I]$	Time (min)	Conv. (MVL%) ^b	Conv. (CL%) ^b	$M_{n, theo}$ (kDa) ^c	$M_{n, SEC}$ (kDa) ^d	\bar{D} ^d
1	50/50/1/1.5/1	10	98.5	94.5	11.0	10.6	1.16
2	75/75/1/1.5/1	15	98.3	96.1	16.6	15.9	1.19
3	100/100/1/1.5/1	20	94.7	91.9	21.2	20.6	1.18
4	125/125/1/1.5/1	25	97.8	88.9	26.5	25.6	1.13
5	150/150/1/1.5/1	30	98.8	90.0	32.1	30.6	1.15
6	200/200/2/3/1	50	98.5	95.2	43.8	32.1	1.18

^a Conditions: 0.02 mmol Benzyl alcohol (BnOH) was used as the initiator. The copolymerizations were conducted at $[MVL]_0 = 4$ M at 0 °C in TOL. ^b Monomer conversions were determined by ¹H NMR. ^c Theoretical molecular weight was calculated from the feeding molar ratio and monomer conversion as $M_{n, theo} = [MVL]/[I] * Conv.(MVL) * MW(MVL) + [CL]/[I] * Conv.(CL) * MW(CL) + MW(Initiator)$. ^d Determined by SEC in THF relative to PS standards.

Table S3. The copolymerization results of MVL with CL for reactivity ratios determination. ^a

Run	[MVL] ₀	[CL] ₀	Conv. ^b (MVL%)	Conv. ^b (CL %)	[MVL] ^c	[CL] ^c	Y ^d	G ^e	F ^e
1	0.49	3.51	30.5	2.7	0.34	3.42	1.58	0.05	0.01
2	1.24	2.76	20.1	2.4	0.99	2.70	3.78	0.33	0.05
3	2.03	1.97	22.0	2.7	1.58	1.92	8.38	0.90	0.13
4	2.80	1.20	6.2	0.8	2.63	1.19	17.86	2.20	0.30
5	3.57	0.43	17.2	2.3	2.96	0.42	61.30	8.17	1.13

^a Conditions: 8 μmol *t*Bu-P₂ was used. [MVL + CL]₀/[*t*Bu-P₂]/[U3]/[BnOH] = 200/0.1/0.15/1. The copolymerizations were conducted at 0°C with a total monomer concentration of 4 M in TOL and then quenched within 10 s. ^b Monomer conversions were measured by ¹H NMR spectra. ^c [MVL] = [MVL]₀ * (1-Conv.(MVL)), [CL] = [CL]₀ * (1-Conv.(CL)). ^d Y = dMVL/dCL = Incorp.(MVL)/Incorp.(CL), dMVL and dCL can be expressed by the content of MVL and CL in the polymer, respectively. ^e G and F are defined as: G = X * (Y-1) / Y and F = X² / Y. According to the Finemann-Ross equation, the reactivity ratios of monomers can be found by the equation: G = F * r_{MVL} - r_{CL}.

Table S4. The quantitative calculation results of sequence distribution for P(MVL-*co*-CL) copolyesters with varied MVL incorporations ^a

Incorp. (MVL, mol%)	CL repeating unit		MVL repeating unit	
	CL-MVL (mol%)	CL-CL (mol%)	MVL-MVL (mol%)	MVL-CL (mol%)
32	10.8	55.7	21.8	11.8
51	10.6	32.0	46.1	11.3
71	8.5	18.4	64.7	8.4

^a The calculations were based on the peak integrals from the region of 63 to 65 ppm in the ¹³C NMR spectra. Samples were prepared according to the conditions shown in Table 2 (runs 2-4).

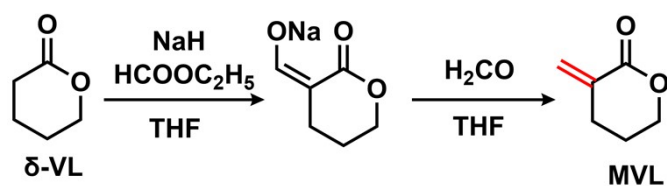
Table S5. TGA results of P(MVL-*co*-CL) copolyesters with varied MVL incorporations ^a

Run	Sample	Incorp. (MVL, mol%)	M _n (kDa) ^c	D ^c	T _{d, 5%} (°C)	T _{d, max} (°C)
1	PCL	0	9.1	1.59	408.3	442.8
2	P(MVL) _{ROP}	100	10.4	1.19	309.0	414.0
3	P(MVL- <i>co</i> -CL)-1	32	22.7	1.16	321.7	424.4
4	P(MVL- <i>co</i> -CL)-2	51	20.6	1.18	282.2	417.7
5	P(MVL- <i>co</i> -CL)-3	71	20.4	1.13	268.5	417.9

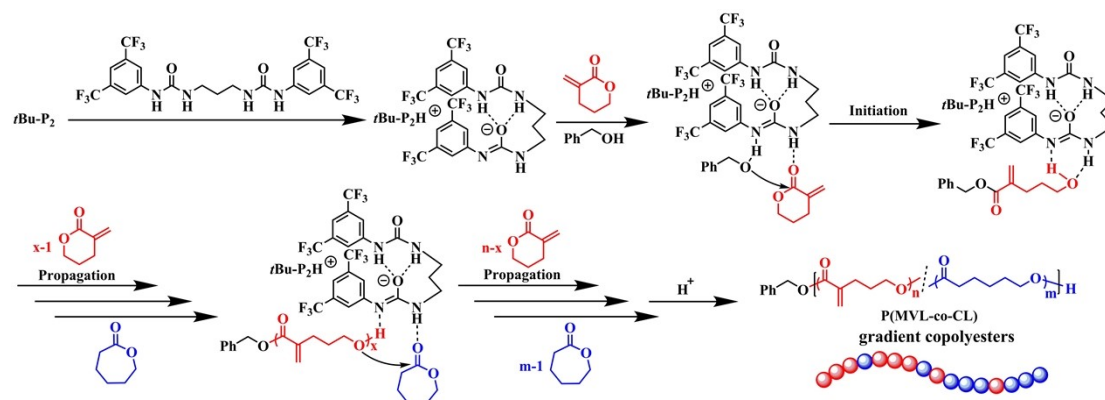
^a P(MVL-*co*-CL)-1 (Table 2, run 2); P(MVL-*co*-CL)-2 (Table 2, run 3); P(MVL-*co*-CL)-3 (Table 2, run 4).

Table S6. DSC results of P(MVL-*co*-CL) copolyesters with varied MVL incorporations

Run	Incorp. (MVL, mol%)	M_n (kDa) ^c	Cooling scan			second heating scan			
			T _c (°C)	ΔH _c (J/g)	T _g (°C)	T _{m1} (°C)	ΔH _c (J/g)	T _{m2} (°C)	ΔH _c (J/g)
1	0	9.1	36.6	77.6	-	53.7	72	-	-
2	10	21.6	20.1	49.8	-61.2	48.8	1.69	53.4	1.67
3	32	22.7	-0.37	41.2	-57.7	39.6	3.20	49.3	23.8
4	51	20.6	-17.3	32.0	-56.6	42.7	18.2	59.7	15.9
5	71	20.4	5.6	25.3	-55.5	70.6	50.2	-	-
6	91	19.1	21.4	50.1	-48.3	75.7	48.6	-	-
7	100	10.4	29.7	60.8	-	78.6	59.5	-	-



Scheme S1. The preparation of MVL from bio-renewable δ -valerolactone (δ -VL) via a two-step protocol.



Scheme S2. Proposed Mechanism for the ROCP of MVL with CL mediated by $t\text{Bu-P}_2/\text{U3}$ binary catalyst.

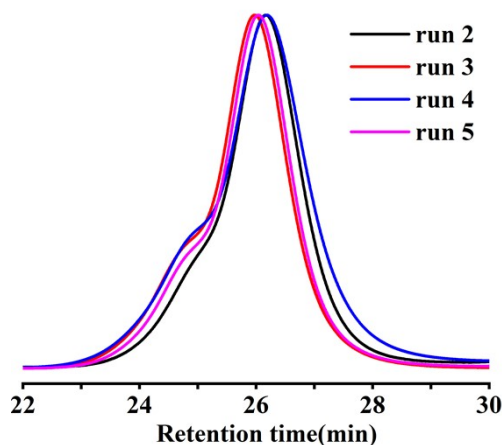


Figure S1. SEC curves of copolymers prepared from four different catalysts (Table 1, runs 2-5).

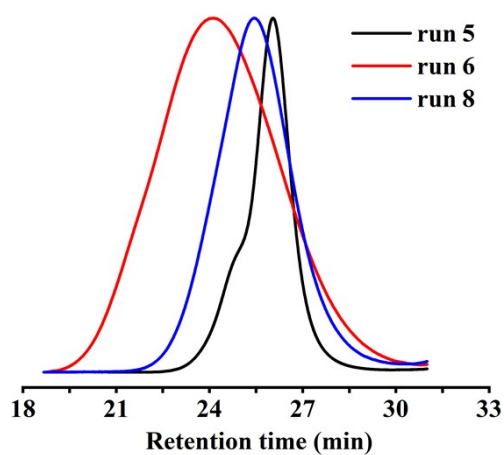


Figure S2. SEC curves of copolymers prepared from three different ureas (Table 1, run 5, 6 and 8).

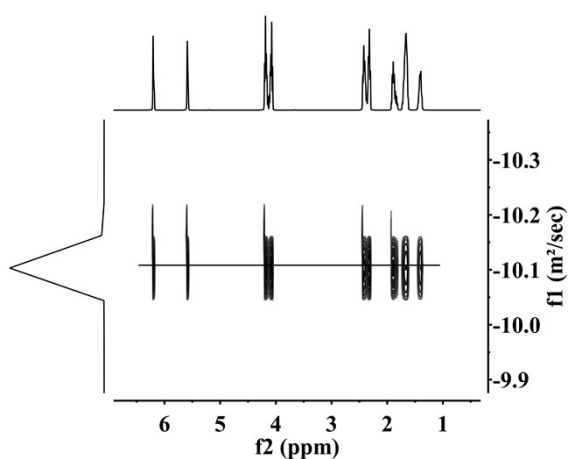


Figure S3. Representative 2D DOSY NMR spectrum of P(MVL-*co*-CL) copolyester measured in CDCl₃ (Table 1, run 10).

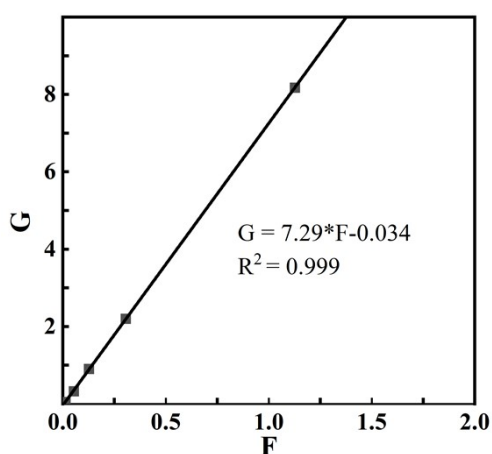


Figure S4. The plot for the determination of reactivity ratios according to Fineman-Ross equation (data shown in Table S3).

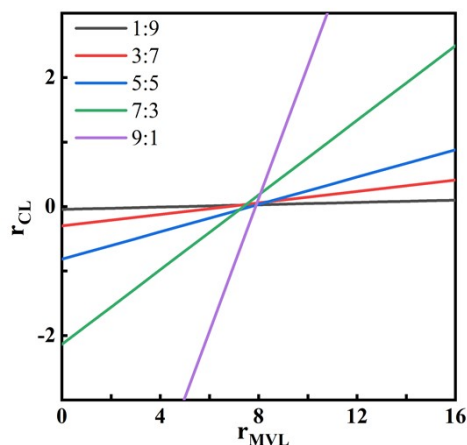


Figure S5. The plot for the determination of reactivity ratios according to Mayo-Lewis equation

$$r_{MVL} = \frac{\lg\left(\frac{[MVL]_0}{[MVL]} - \frac{1}{p} \lg\left\{\frac{1 - p([CL]/[MVL])}{1 - p([CL]_0/[MVL]_0)}\right\}\right)}{\lg\left(\frac{[CL]_0}{[CL]} + \lg\left\{\frac{1 - p([CL]/[MVL])}{1 - p([CL]_0/[MVL]_0)}\right\}\right)}, \quad p = \frac{1 - r_{CL}}{1 - r_{MVL}}$$

(data shown in Table S3). The reactivity ratios of MVL and CL was determined to be $r_{MVL} = 7.68$ and $r_{CL} = 0.035$.

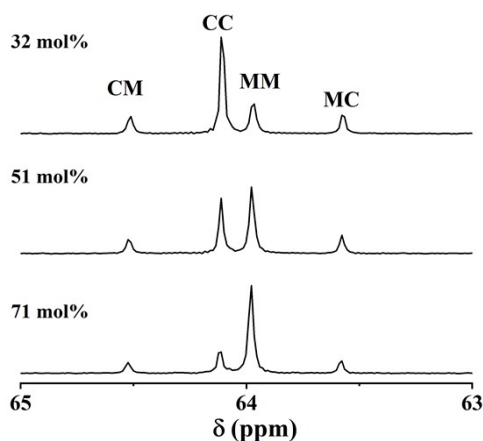


Figure S6. The enlargement region from 63 to 65 ppm of the ^{13}C NMR spectra (32 mol%: Table 2, run 2; 51 mol%: Table 2, run 3; 71 mol%: Table 2, run 4).

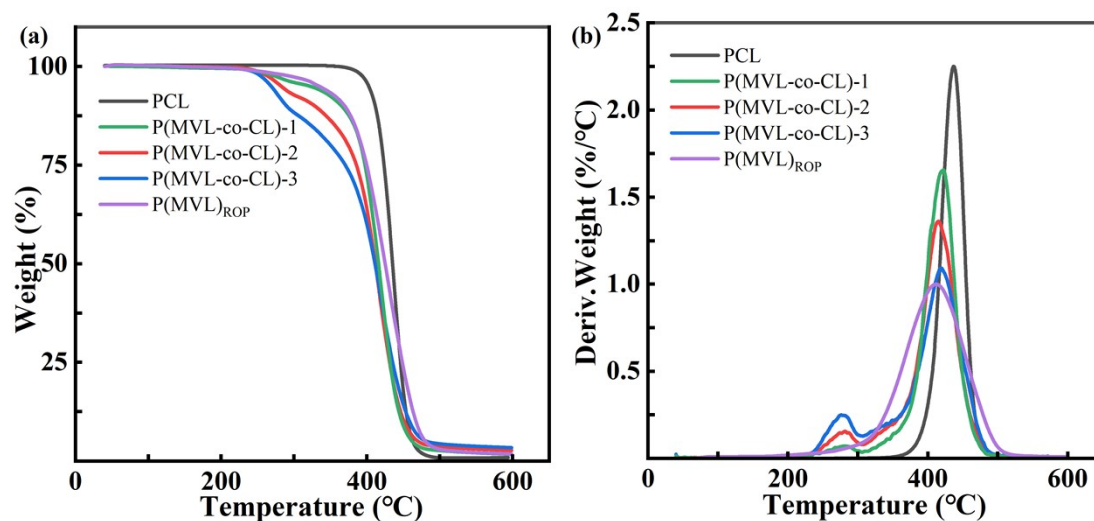


Figure S7. (a) TGA and (b) DTG curves for P(MVL-*co*-CL) copolyesters with various MVL incorporations as well as PCL and PMVL homopolyester for comparison (PCL: $M_n = 9.1$ kDa, $D = 1.59$; P(MVL-*co*-CL)-1: 32 mol% MVL, Table 2, run 2; P(MVL-*co*-CL)-2: 51 mol% MVL, Table 2, run 3; P(MVL-*co*-CL)-3: 71 mol% MVL, Table 2, run 4; P(MVL)_{ROP}: $M_n = 10.4$ kDa, $D = 1.19$).

References

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