Supporting Information

Lignin-grafting alternative copolymer of 3,4-dihydrocoumarin and epoxides as an active and flexible ingredient in sunscreen

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1.0 Experimental details

1.1 Details of ^{31}P NMR test method

20 mg of lignin was dissolved in anhydrous pyridine and deuterated chloroform (500 μL, 1.6:1, v/v). Then, the internal standard solution (100 μL, 0.1212 mol/L, internal N-hydroxy-5-norbornene-2,3-dimethylidene imide in Py-D_5/$CDCl_3$) and chromium acetylacetonate (III) (25 μL, 0.0312 mol/L) as the relaxation reagent were added. The mixture was reacted with 100 μL of a phosphating reagent (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholate, TMDP) for 10 min and transferred into a 5 mm NMR tube, which was subsequently analyzed for ^{31}P NMR spectra on Bruker AVANCE III 400 MHz.

1.2 Antioxidation assay details

First, EHL-*g*-P(DHC-*alt*-SO) solutions with different concentrations (0.1, 0.5, 1, and 5 mg/ mL) were prepared in DMF. DPPH was dissolved in ethanol to form a dark purple solution of 0.1 mM and stored in a dark environment. 25 μL EHL-*g*-P(DHC-*alt*-SO) solutions of different concentrations were added to 200 μL DPPH ethanol solution and stored in the dark. Absorbance at 517 nm was measured at different time intervals using a microplate reader (Epoch, Biotek, USA). The ELISA plate was heated by a microporous plate thermostatic oscillator (BE-9010, China). The blank group was 200 μL ethanol solution containing 25 μL EHL-*g*-P(DHC-*alt*-SO), and the control group was 200 μL DPPH ethanol solution containing 25 μL DMF. Three groups of parallel experiments were set for each test, and the average value was taken at last.

1.3 Cytotoxicity assay details

L929 cells (mouse fibroblast cell line, provided by Zhi's group, Southwest Jiaotong University) were cultured in the minimum essential medium -α (α-MEM) supplemented with 10% newborn calf serum and 1% penicillin and streptomycin at 37 ℃ and 5% CO_2. LD5S5-3 was used in the cytotoxicity evaluation and cell live/dead staining. Cytotoxicity of LD5S5-3 CCK-8 cell proliferation and cytotoxicity detection kit was determined by in vitro culture method (Beijing China Petroleum & Chemical Corporation limited); LD5S5-3 was first dissolved in DMSO to form a homogeneous solution, and then diluted in proportion with DMSO. 5×10^4 L929 cells were inoculated in 24-well plates. After attachment, 10 μL of DMSO diluted LD5S5-3 solution was added to the medium to reach the corresponding concentrations (0.05, 0.1, 0.2, 0.5 and 1 mg/mL). After culturing for 24 h, the cells were washed 3 times with PBS, placed in a 150 μL culture medium containing 10% CCK-8 solution, and incubated at 37℃ for 4 h. The absorbance at 450 nm was measured by a microplate reader (Epoch, Biotek, USA). Meanwhile, cells cultured in a pure medium were used

as a control group. Cell viability/death staining was also performed. 5×10^4 L929 cells were seeded into 24-well plates. After attachment, different DMSO diluted LD5S5-3 solutions were added to the medium. After culturing for 24 h, washed with PBS 3 times, then stain with Calcein-AM (Sigma, USA) and propidium iodide (PI) (Sigma, USA), and finally photograph with a fluorescence microscope (IX73, Olympus, Japan).

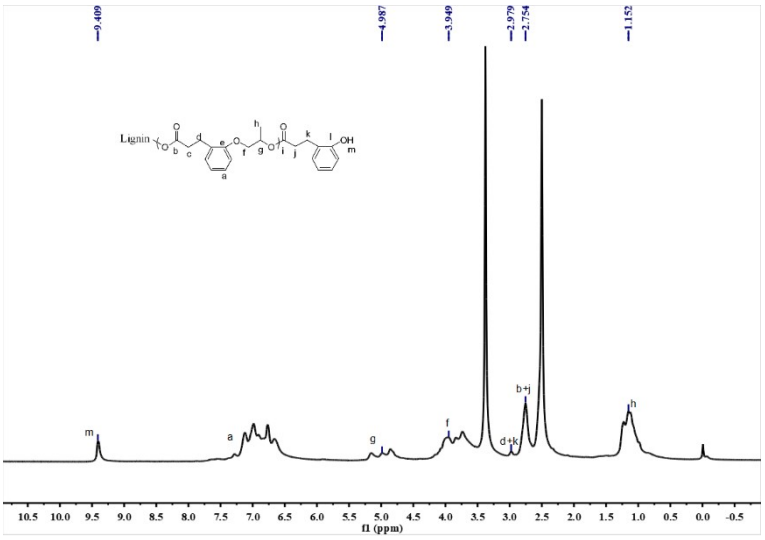


Fig. S1 ^{1}H NMR spectra of LD5P5.

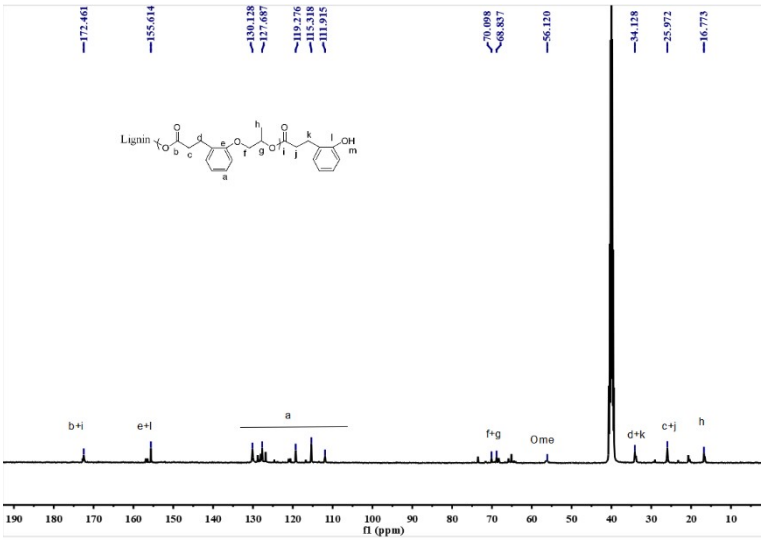


Fig. S2 ^{13}C NMR spectra of LD5P5.

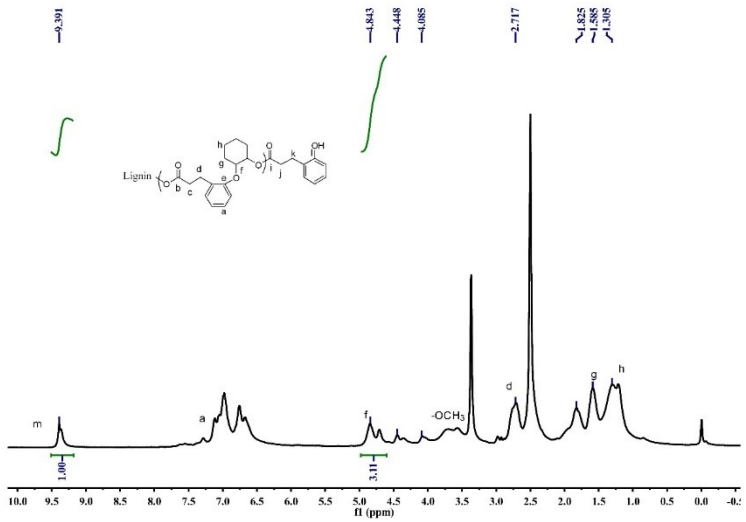


Fig. S3 ^{1}H NMR spectra of LD5C5.

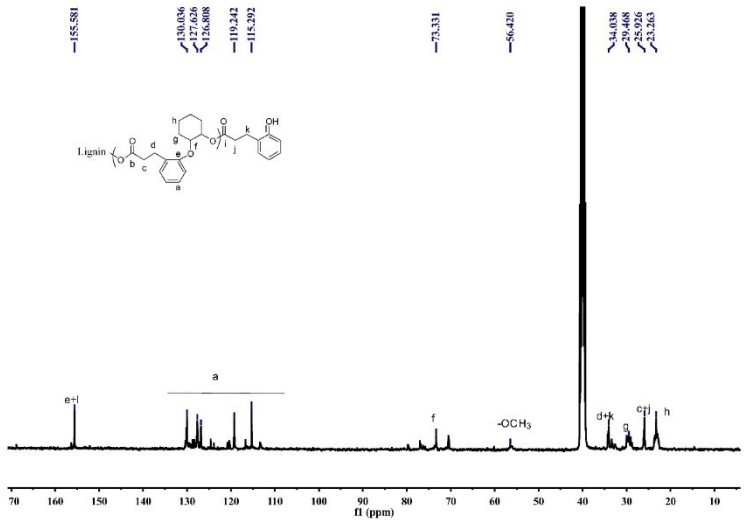


Fig. S4 ^{13}C NMR spectra of LD5C5.

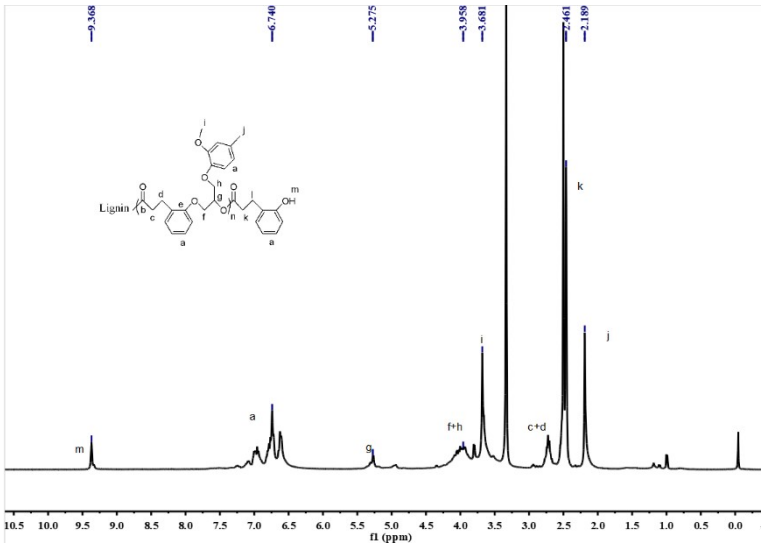


Fig. S5 ^{1}H NMR spectra of LD5MP5.

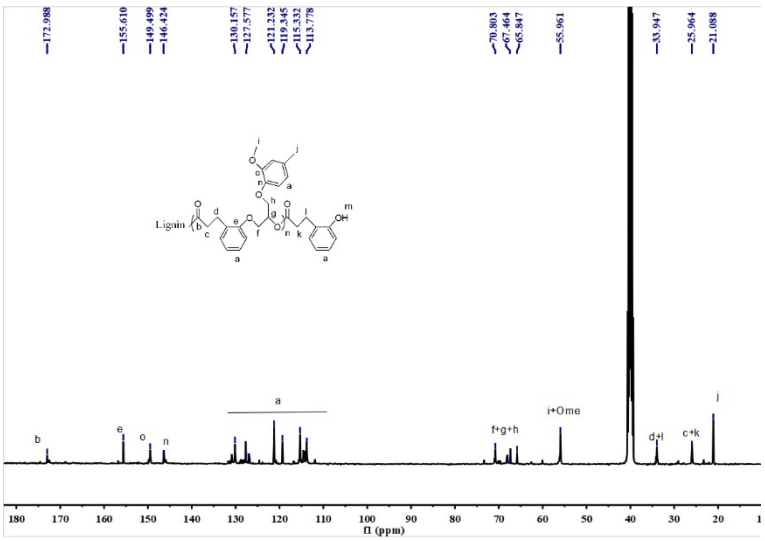
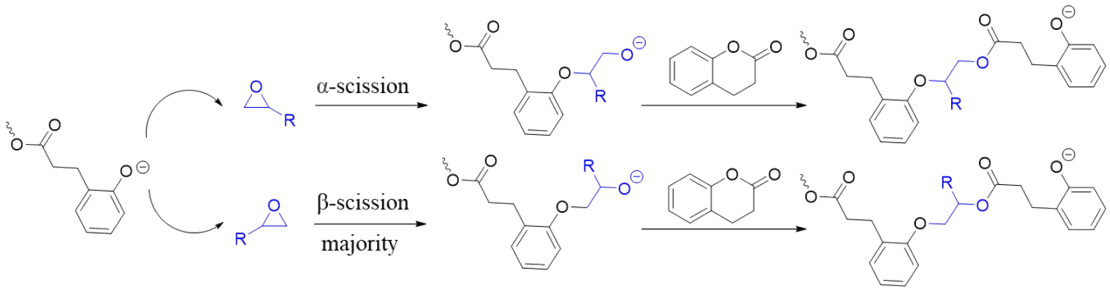


Fig. S6 ^{13}C NMR spectra of LD5MP5.



Scheme S1 β-Scission and α-Scission of Epoxides during the Copolymerization.

Table S1 Molecular weight of EHL-*g*-P(DHC-*alt*-SO) and EHL.

Sample	Mn1	Mw1	ĐM1	Mn2	Mw2	ĐM2	Area %
EHL	805000	2326000	2.89	1500	1980	1.31	52.33/47.67
LD1S1	626000	1159000	1.85	4400	8990	2.04	24.15/75.85
LD3S3	428000	581000	1.38	5700	7300	1.29	51.12/48.78
LD5S5-1	135000	223000	1.64	6200	6680	1.06	62.15/37.84
LD5S5-2	632000	701000	1.11	16800	17900	1.06	49.77/50.23
LD5S5-3	629000	793000	1.26	1790	5090	2.83	9.48/90.52
LD5S5-4	129000	191000	1.46	3000	4820	1.57	99.94/0.06
LD10S10	920000	1079000	1.17	1400	3110	2.22	3.09/96.91

Table S2 Solubility of EHL-*g*-P(DHC-*alt*-SO) in various solvents.

Entries	Solubility [a]					
	DMSO	THF	Dichloromethane	Chloroform	Methanol	Ethyl acetate
LD5S5-1	+	+	+	+	±	±
LD5S5-2	+	+	+	+	±	±
LD5S5-3	+	+	+	+	±	±
LD5S5-4	+	+	+	+	±	±
LD1S1	±	±	±	±	±	±
LD3S3	+	+	+	+	±	±
LD10S10	+	+	+	+	±	±

[a] "+" stands for soluble and "±" stands for swollen; usually, 100 mg sample was added into 0.5 mL solvent and kept for 1 h for the solubility test at room temperature.

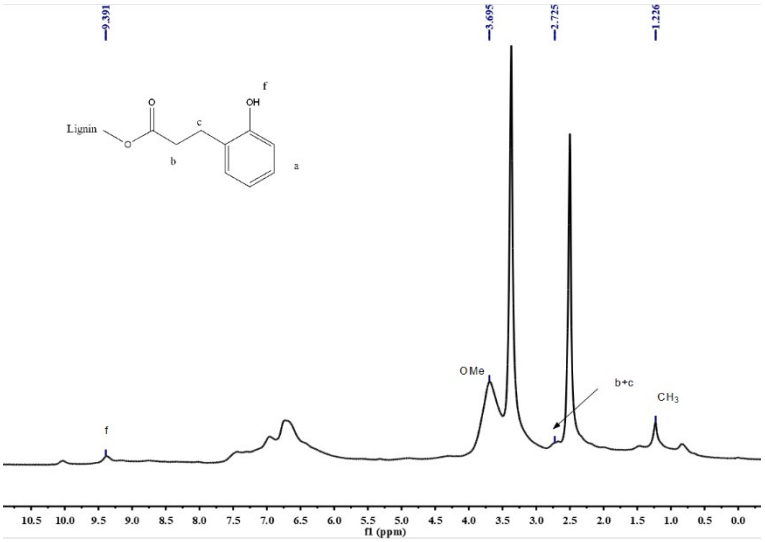


Fig. S7 [1] H NMR spectra of LD1S0.

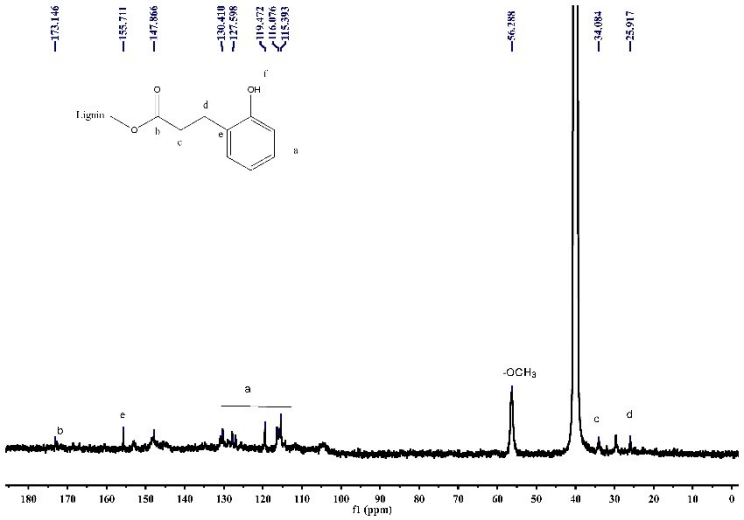


Fig. S8 ^{13}C NMR spectra of LD1S0.

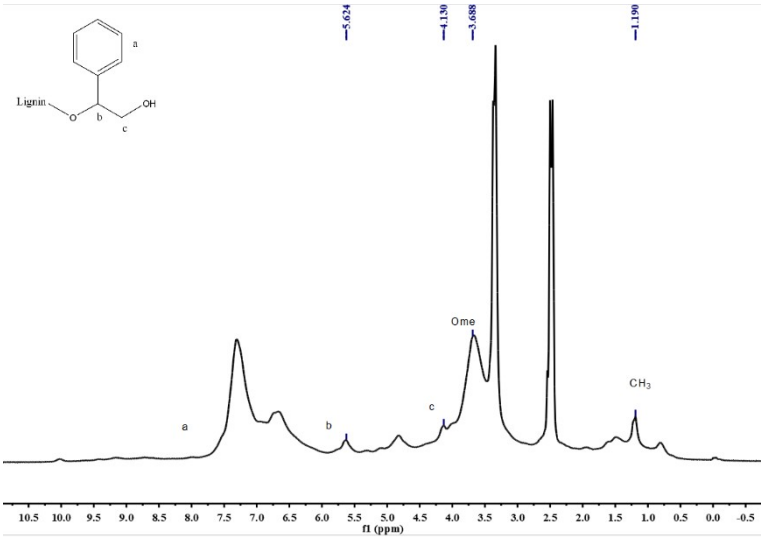


Fig. S9 ^{1}H NMR spectra of LD0S1.

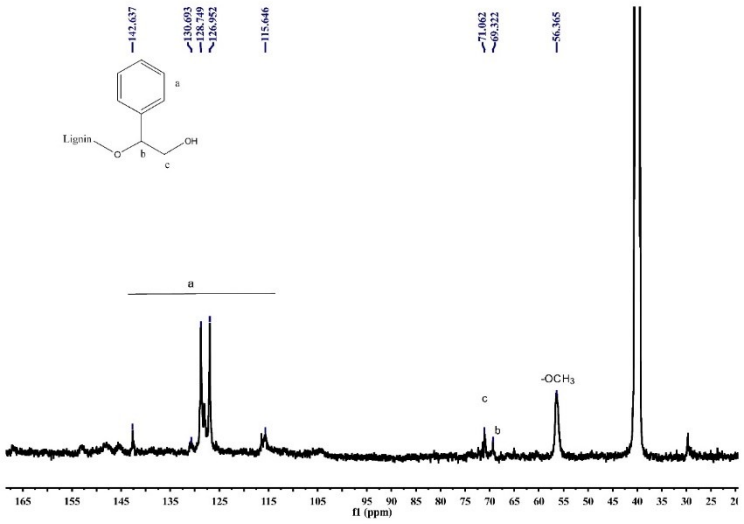


Fig. S10 ^{13}C NMR spectra of LD0S1.

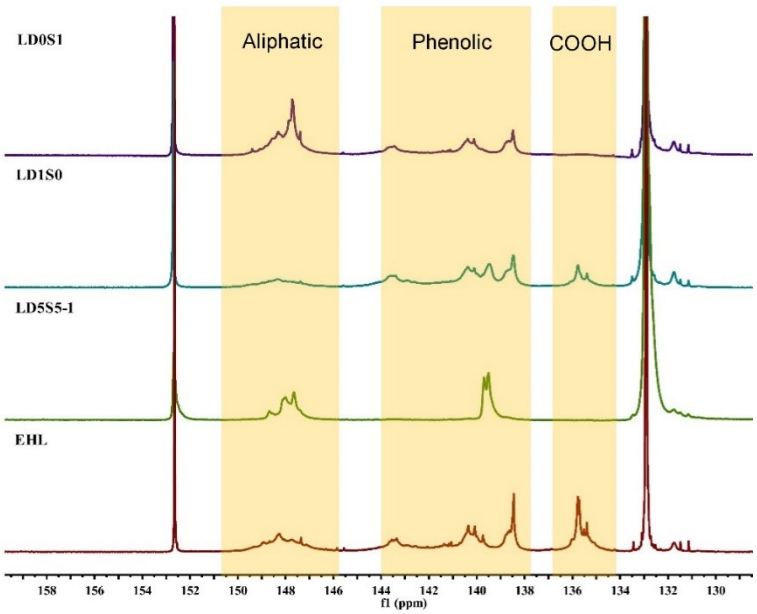


Fig. S11 ^{31}P NMR spectra of EHL, LD5S5-1, LD1S0 and LD0S1.

Table S3 The hydroxyl contents of lignin before and after grafting copolymerization were examined by ^{31}P NMR.

Sample	Hydroxyl content (mmol/g lignin)			
	Aliphatic	Phenolic	Carboxylic	Total
EHL	0.7379	1.7931	0.9332	3.4656
LD5S5-1	0.4424	0.7757	0	1.2181
LD1S0	0.0909	1.9877	0.3511	2.7204
LD0S1	1.4847	0.8968	0	2.3815

Table S4 Thermal properties of EHL and EHL-*g*-P(DHC-*alt*-EPOs).

Entries	$T_{d\text{-}5\%}$	T_g
EHL	233.1°C	157.5°C
LD5S5-3	210.8°C	16.0°C
LD1S1	252.4°C	125.4°C
LD3S3	218.9°C	29.1°C
LD10S10	194.82°C	-3.6°C
LD5P5	231.8°C	12.4°C
LD5C5	214.5°C	15.6°C
LD5MP5	220.7°C	-1.4°C

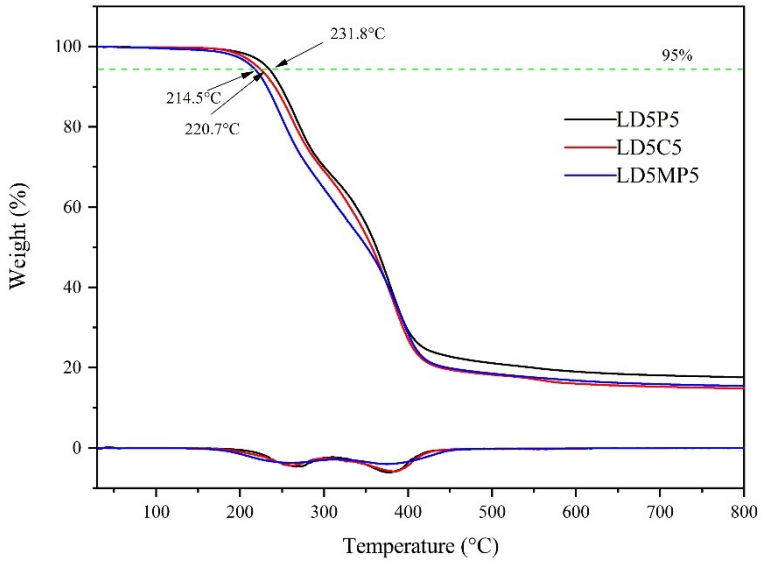


Fig. S12 TG and DTG of LD5P5, LD5C5, and LD5MP5.

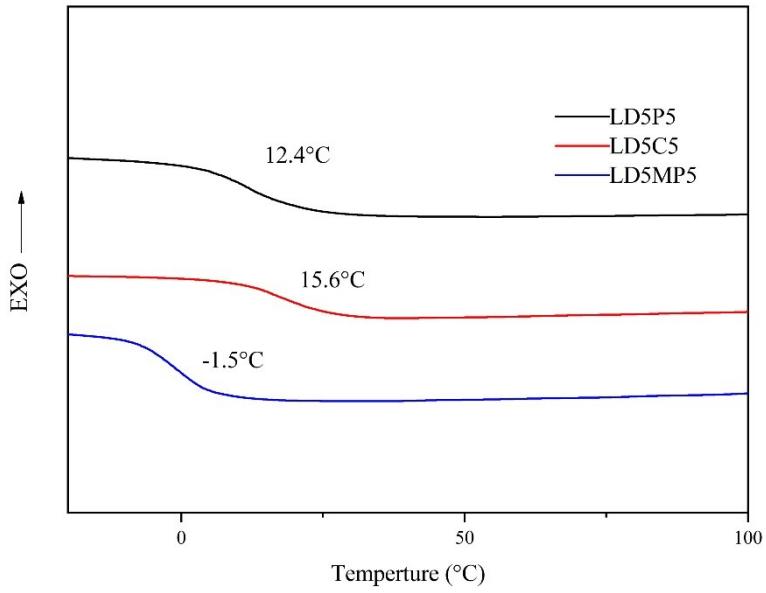


Fig. S13 DSC curves of LD5P5, LD5C5, and LD5MP5.

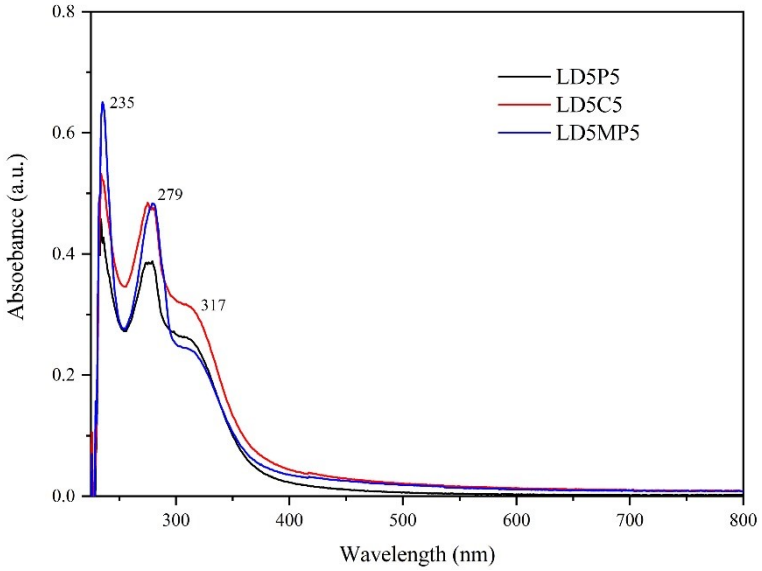


Fig. S14 UV-Vis absorption curves of LD5P5, LD5C5, and LD5MP5.

Table S5 The kinetic parameters for EHL-*g*-P(DHC-*alt*-SO) to DPPH.

Concentration of LDS		Reaction temperature T(°C)	Pseudo-first order reaction kinetic equation		Pseudo-second order kinetics equation	
		□	$k_1(min^{-1})$	R^2	$k_3((mMol/L)^{-1}min^{-1})$	R^2
LD5S5-3	0.1mg/mL	25	-0.02075	0.84875	0.03428	0.89095
LD5S5-3	0.5mg/mL	25	-0.02365	0.85988	0.04325	0.90795
LD5S5-3	1mg/mL	25	-0.02114	0.86878	0.03935	0.91376
LD5S5-3	5mg/mL	25	-0.10676	0.99723	0.53111	0.93828
LD3S3	0.5mg/mL	25	-0.02499	0.86651	0.07637	0.91745
LD1S1	0.5mg/mL	25	-0.04917	0.90557	0.24235	0.97611
LD5S5-3	0.5mg/mL	35	-0.0288	0.85355	0.0605	0.91292
LD5S5-3	0.5mg/mL	45	-0.0496	0.91053	0.22614	0.96288

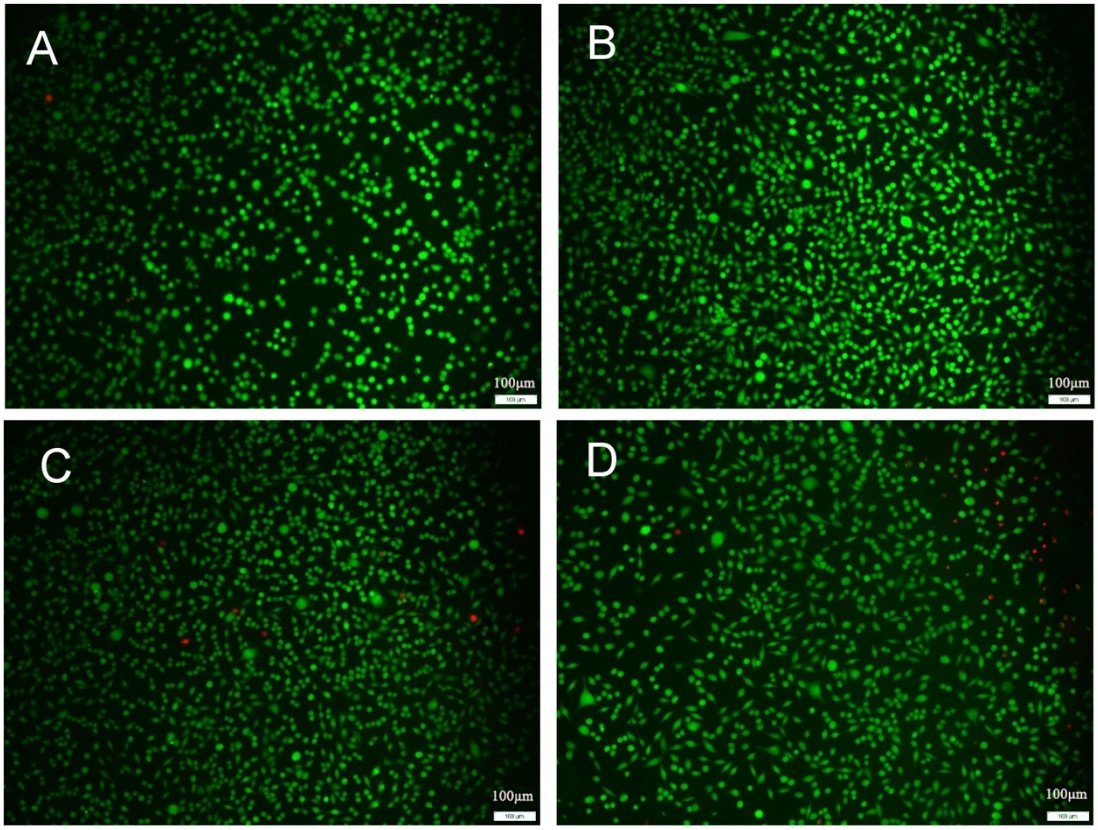


Fig. S15 Fluorescent images of L929 cells stained by Calcein-AM (green) and PI (red) treated with 0.05 mg/mL LD5S5-3 (A); treated with 0.1 mg/mL LD5S5-3 (B); treated with 0.2 mg/mL LD5S5-3 (C); treated with 1 mg/mL LD5S5-3 (D).

Table S6 Comparison of SPF of lignin-based materials

code	materials	method	SPF
1[1]	lignin	/	5.72
2[2]	Sodium lignosulfonate + methacrylate	ATRP	2.45
3[3]	alkali lignin + vinyl benzophenone	ATRP	18
4[4]	Lignosulfonate + TiO_2	Self-assembly	15.57
5[5]	alkali lignin + 2,4-dihydroxybenzophenone	Self-assembly	22.31
6[6]	Lignosulfonate + catechol	Self-assembly	27

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3. Y. Wu, Y. Qian, A. Zhang, H. Lou, D. Yang and X. Qiu, *Ind. Eng. Chem. Res.*, 2020, **59**, 17057-17068.
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