Supporting Information

Antioxidant and adsorption properties of bio-inspired phenolic polymers: a comparative study of catechol and gallol

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Experimental section

Materials. 3,4-Dimethoxybenzaldehyde (DMB) and 4-methoxystyrene (MS) were purchased from Tokyo Chemical Industry and used as received. 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT), 2-cyano-2-propyl dodecyl trithiocarbonate (CPDTTC) and 4-cyano-4-[(dodecylsulfanyl-thiocarbonyl)sulfanyl] pentanoic acid (CDSPA) were purchased from Sigma-Aldrich and used as received.

Synthesis of 3,4-dimethoxystyrene (DMS). The same procedure as TMS was used, except the TMB replaced with DMB (9.19 g, 55.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): (δ, ppm) 6.94 (d, 1H, J=1.6 Hz), 6.90 (dd, 1H, J=9.6 Hz, J'=1.6 Hz), 6.76 (d, 1H, J=9.6 Hz), 6.62 (dd, 1H, J=17.7 Hz, J'=10.8 Hz), 5.59 (dd, 1H, J=17.7 Hz, J'=0.9 Hz), 5.12 (dd, 1H, J=10.8 Hz, J'=0.9 Hz), 3.85 (s, 3H), 3.82 (s, 3H).

Synthesis of poly(3,4-dimethoxystyrene) (PDMS). The same procedure outlined for PTMS was used except the TMS replaced with DMS (1.7 g, 10.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): (δ, ppm) 7.0–5.9 (Ar-H), 4.1–3.4 (OCH_3), 3.3–3.0 (CH_2-S), 2.4–2.2 (CH_2-CN), 1.2–0.7 ($C_{10}H_{20}$-CH_3), 2.4–0.9 (CH(Ar)-CH_2).

Synthesis of poly(4-methoxystyrene) (PMS). The same procedure outlined for PMS was used, except with the TMS replaced with MS (1.38g, 10.3mmol). ^{1}H NMR (400 MHz, $CDCl_3$): (δ, ppm) 7.1–6.2 (Ar-H), 3.9–3.6 (OCH_3), 3.3–3.1 (CH_2-S), 2.4–2.2 (CH_2-CN), 1.2–0.8 ($C_{10}H_{20}$-CH_3), 2.4–1.0 (CH(Ar)-CH_2).

Demethylation of PDMS to poly(3,4-dihydroxystyrene) (PVCat).[1] The same procedure used to prepare PVGal was used to prepare PVCat, except that the PTMS was replaced with PDMS (0.82 g, 5 mmol). ^{1}H NMR (400 MHz, DMSO-d6): (δ, ppm) 9.1–7.6 (OH), 6.8–5.5 (Ar-H), 2.2–0.7 (CH(Ar)-CH_2).

Demethylation of PMS to poly(4-hydroxystyrene) (PVPh).[2] The same procedure as PVGal was used, except that the PTMS was replaced with PMS (0.67 g, 5 mmol). ^{1}H NMR (400 MHz, DMSO-d6): (δ, ppm) 9.2–8.5 (OH), 7.2–5.7 (Ar-H), 2.4–0.7 (CH(Ar)-CH_2).

ORAC Assay. The ORAC assay was performed according to the method of a previous report[3] using fluorescein as the substrate and AAPH as the oxidant generator. 1.8 mL of fluorescenin (final concentration is 70 nM) buffer solution (67 mM phosphate buffer, pH 7.4) and 0.3 mL of sample methanol solution (final concentration is 10 μM based on the monomer unit) were mixed in a quartz cuvette spectrophotometer cell. Then, 0.9 mL of AAPH (final concentration is 18 mM) buffer solution (67 mM phosphate buffer, pH 7.4) were added, and fluorescence intensities were recorded every 2 seconds for 60 min at excitation and emission wavelengths of 468 and 520 nm, respectively. The calibration curve was made by measuring a blank sample solution containing 0.3 mL of methanol and four calibration solutions of trolox (final concentrations of trolox were 1, 3, 5 and 7 μM). The area under the curve (AUC) was calculated by integrating the relative fluorescence curve. The net AUC of the sample was calculated by the subtracting the AUC of the blank. The regression equation between net AUC and trolox concentration was determined, and the ORAC values were expressed as μmol trolox equivalent of sample using the trolox standard curve."

Table S1 Effect of CTAs on the polymerization of TMS. The feed ratio of [TMS]/[CTA]/[AIBN] was 30/1/1; TMS/THF (mL/mL) was 1/2.

Target D_p	CTA[a]	M_n[b] (g mol^{-1})	D_p[b]	M_w/M_n[b]
30	None	15,800	80	2.3
30	DDMAT	3,500	16	1.4
30	CDTTC	5,800	29	1.2
30	CPDTTC	3,800	18	1.2
30	CDSPA	3,800	18	1.6

[a] "None" indicates the free-radical polymerization. [b] Calculated by size-exclusion chromatography using polystyrene standards; chloroform was used as the eluent.

Table S2 Effect of concentration on the polymerization of TMS in tetrahydrofuran (THF). The amount of solvent was varied from 1/4 to 1/1 (TMS/THF, mL/mL); the feed ratio of [TMS]/[CTA]/[AIBN] was fixed at 30/1/1.

Target D_p	TMS/THF (mL mL^{-1})	M_n[a] (g mol^{-1})	D_p[a]	M_w/M_n[a]
30	1/4	6,300	31	1.3
30	1/2	5,800	29	1.2
30	1/1.5	4,900	24	1.2
30	1/1	5,500	27	1.1

[a] Calculated by SEC using polystyrene standards; chloroform was used as the eluent.

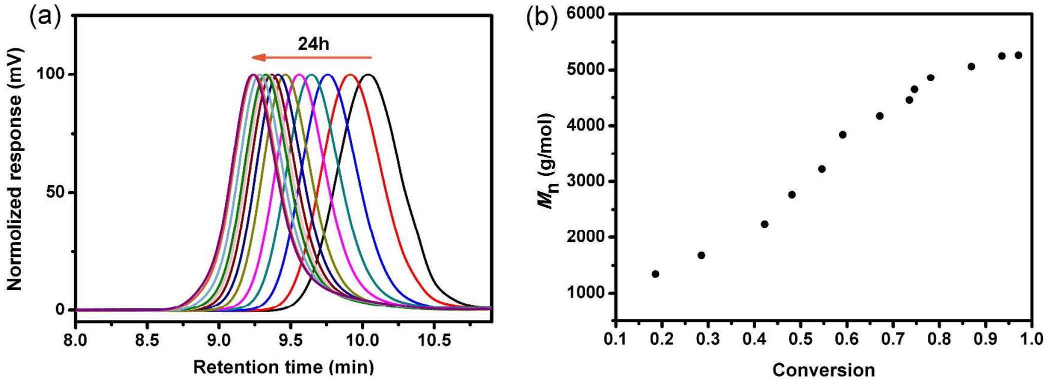


Figure S1 (a) SEC traces and (b) plot of M_n versus monomer conversion during RAFT polymerization of TMS in THF with a feed ratio of [TMS]/[CDTTC]/[AIBN] = 30/1/1.

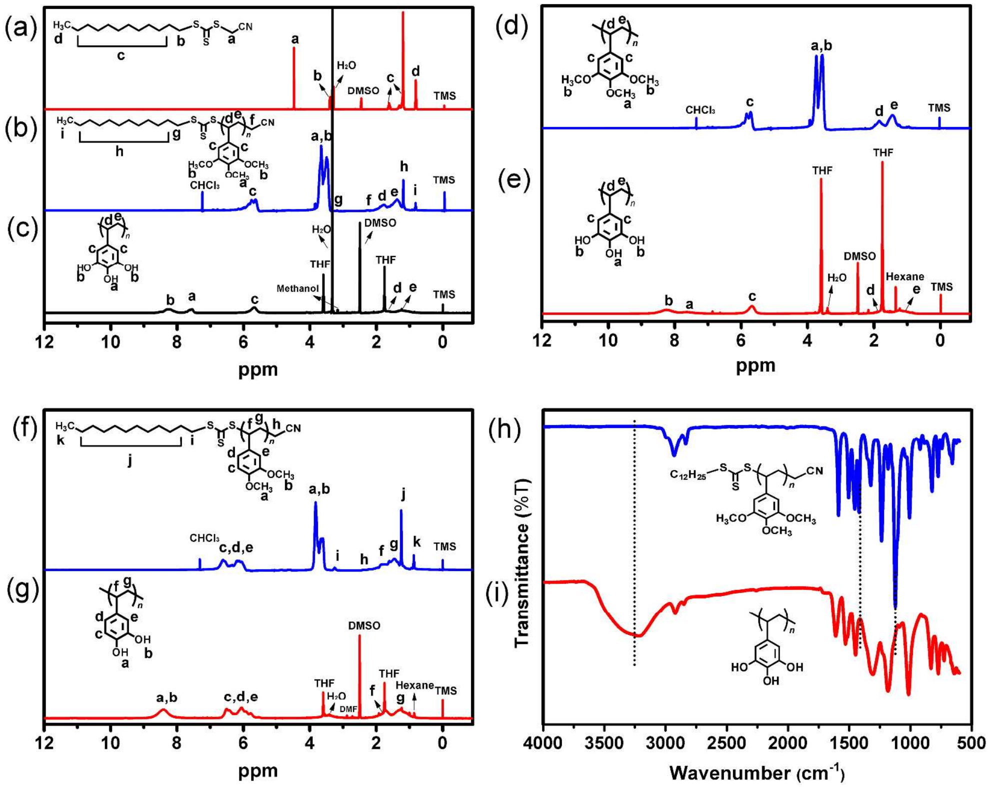
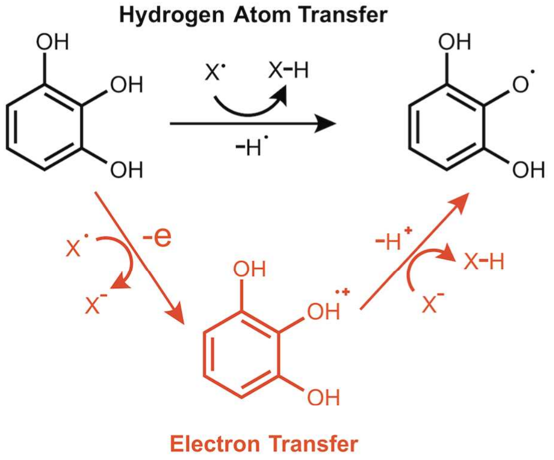


Figure S2 ^{1}H NMR spectra of CDTTC (a), PTMS synthesized via RAFT polymerization (b), PVGal synthesized from the RAFT-polymerized PTMS (c), PTMS synthesized via free-radical polymerization (d), PVGal synthesized from the free-radical-polymerized PTMS, PDMS (f), and PVCat (g). ATR-FTIR spectra of PTMS (h) and PVGal (i).



$X^{\cdot}$ = 2,2-diphenyl-1-picrylhydrazyl radical

Figure S3 Possible mechanisms of radical scavenging by gallol groups.

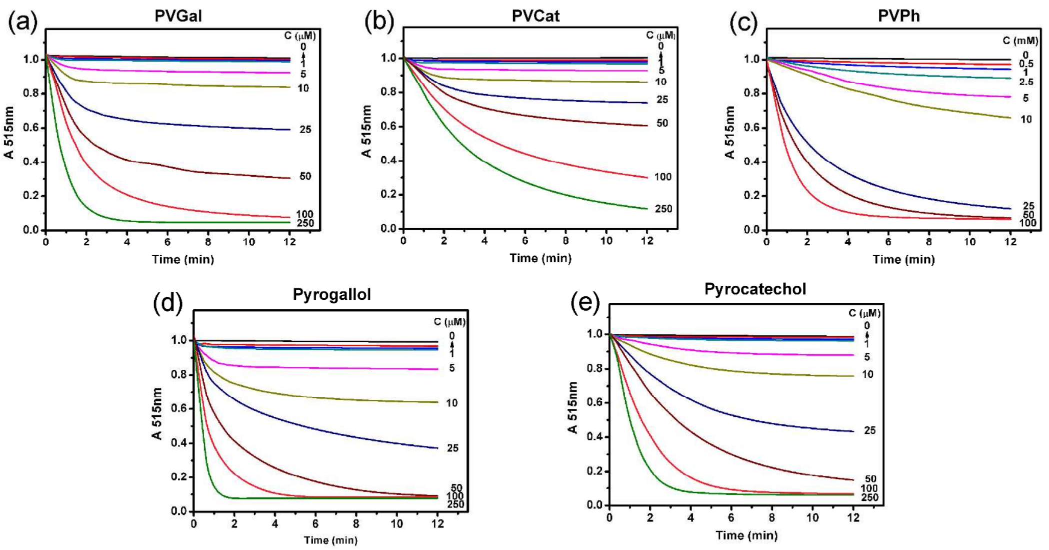


Figure S4 DPPH decoloration kinetics for the tested antioxidants: PVGal (a), PVCat (b), PVPh (c), pyrogallol (d), and pyrocatechol (e)

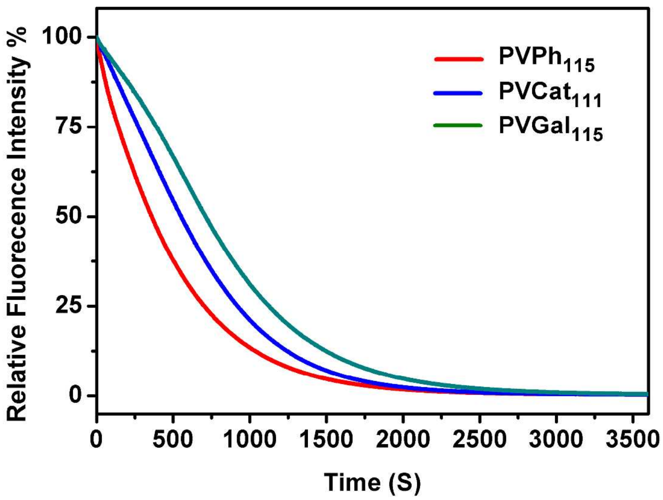


Figure S5 Fluorescence intensity curve of fluorescein in the presence of phenolic polymers ($PVPh_{115}$, $PVCat_{111}$ and $PVGal_{115}$).

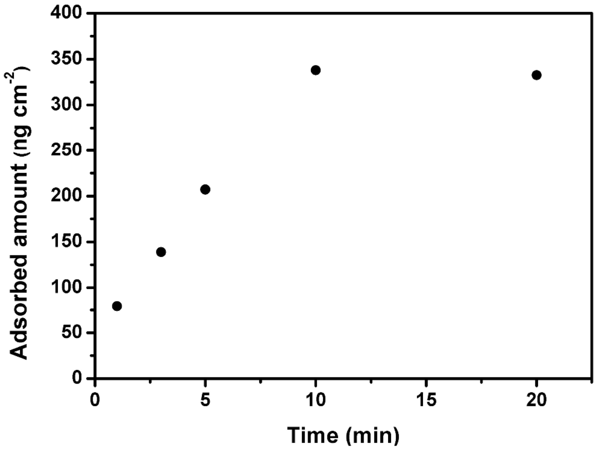


Figure S6 Adsorbed amounts of PVGal$_{115}$ (1 mg mL^{-1}) on Au substrate versus immersion time.

REFERENCES

(1) Isakova, A.; Topham, P. D.; Sutherland, A. J., Controlled RAFT polymerization and Zinc binding performance of catechol-inspired homopolymers. *Macromolecules* **2014,** *47* (8), 2561−2568.

(2) Wang, J.; Cheung, M. K.; Mi, Y., Miscibility and morphology in crystalline/amorphous blends of poly(caprolactone)/poly(4-vinylphenol) as studied by DSC, FTIR, and ^{13}C solid state NMR. *Polymer* **2002,** *43* (4), 1357−1364.

(3) Dudonne, S.; Vitrac, X.; Coutiere, P.; Woillez, M.; Mérillon, J. M., Comparative study of antioxidant properties and total phenolic content of 30 plant extracts of industrial interest using DPPH, ABTS, FRAP, SOD, and ORAC assays. *J. Agr. Food Chem.* **2009,** *57* (5), 1768−1774.