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Supporting Information

Ferulic acid-based reactive core-shell latex by seeded emulsion polymerization

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Determination of AC4VG conversion

AC4VG monomer conversions were calculated by ^{1}H NMR using the following equation:

$$conversion\ (AC4VG) = 100 \times \left[1 - \frac{\left(\dfrac{\int_{5.18}^{5.28} CH(AC4VG)_t/1}{\int_{0.72}^{1.01} CH_3(PBA)_t/3} \right)}{\left(\dfrac{\int_{5.18}^{5.28} CH(AC4VG)_{t=0}/1}{\int_{0.72}^{1.01} CH_3(PBA)_{t=0}/3} \right)} \right] \qquad \text{(Equation S1)}$$

Determination of the number of particles in the seed latex and in the composite latex

The number of particles in the seed and final latexes were calculated as follows:

The mass of one polymer particle is calculated as:

$$m_{polymer\ particle} = \frac{\pi}{6}(D_v)^3\rho \qquad \text{(Equation S2)}$$

where,

D_v is the volume-average particle diameter
ρ is the polymer density

The number of particles in a given quantity of latex is calculated as:

$$N_p = \frac{m_{polymer}}{m_{polymer\ particle}} \qquad \text{(Equation S3)}$$

where,

$m_{polymer}$ is the mass of polymer in the latex
$m_{polymer\ particle}$ is the mass of one polymer particle

For the P(S-*co*-BA) latex, using the volume-intensity average diameter of 55 nm, as measured by DLS,

$$m_{P(S\text{-}co\text{-}BA)\ particle} = \frac{\pi}{6}(55nm)^3\left(\frac{1.058\ g}{cm^3}\right)\left(\frac{10^{-7}cm}{nm}\right)^3 = 9.2 \times 10^{-17}g$$

In 16 g of P(S-*co*-BA) seed latex at 8 wt. % solids content,

$$N_p\ in\ P(S\text{-}co\text{-}BA)\ seed\ latex = \frac{(16g)(0.08)}{9.2 \times 10^{-17}g} = 1.4 \times 10^{16}$$

For the P(S-*co*-BA)@PAC4VG latex, using the volume-intensity average diameter of 74 nm, as measured by DLS,

$$m_{P(S\text{-}co\text{-}BA)@PAC4VG\ particle} = \frac{\pi}{6}(74nm)^3\left(\frac{1.022\ g}{cm^3}\right)\left(\frac{10^{-7}cm}{nm}\right)^3 = 2.2 \times 10^{-16}g$$

With the near complete conversion of 2 g of AC4VG in the seed latex,

$$N_p\ in\ P(S\text{-}co\text{-}BA)@PAC4VG\ latex = \frac{(16g)(0.08) + 2g}{2.2 \times 10^{-16}g} = 1.5 \times 10^{16}$$

For the PBA latex, using the volume-intensity average diameter of 60 nm as measured by DLS,

$$m_{PBA\ particle} = \frac{\pi}{6}(60nm)^3\left(\frac{1.087\ g}{cm^3}\right)\left(\frac{10^{-7}cm}{nm}\right)^3 = 1.2 \times 10^{-16}g$$

In 15 g of PBA seed latex at 8 wt. % solids,

$$N_p\ in\ PBA\ seed\ latex = \frac{(15g)(0.08)}{1.2 \times 10^{-16}g} = 1.0 \times 10^{16}$$

For the PBA@PAC4VG latex, using the volume-intensity average diameter of 91 nm, as measured by DLS,

$$m_{PBA@PAC4VG\ particle} = \frac{\pi}{6}(90nm)^3\left(\frac{1.026\ g}{cm^3}\right)\left(\frac{10^{-7}cm}{nm}\right)^3 = 4.0 \times 10^{-16}g$$

With the near complete conversion of 3 g of AC4VG in the seed latex,

$$N_p\ in\ PBA@PAC4VG\ latex = \frac{(15g)(0.08) + 3g}{4.0 \times 10^{-16}g} = 1.1 \times 10^{16}$$

Determination of the interfacial tensions

The interfacial tensions of the polymers were calculated using Wu's method[34]:

$$\gamma_{ij} = \gamma_i + \gamma_j - \left[\frac{4\gamma_i^P\gamma_j^P}{\gamma_i^P + \gamma_j^P}\right] - \left[\frac{4\gamma_i^D\gamma_j^D}{\gamma_i^D + \gamma_j^D}\right] \qquad \text{(Equation S4)}$$

γ_{ij} is the interfacial surface tension between species *i* and species *j*

γ_i^P, γ_i^D and γ_j^P, γ_j^D are the polar and dispersion components of the surface tension of species *i* and *j* respectively

γ_i and γ_j are the total surface tensions of species *i* and *j* respectively ($\gamma_i^P + \gamma_i^D = \gamma_i$)

In order to use Wu's method, the polar and dispersion components of the surface tensions of each solid species were calculated using Owen's equation[35] (Equation S5; here γ_i^P and γ_i^D are denoted as γ_S^P and γ_S^D in reference to the solid polymer species) by using the measured contact angles of a polar (H_2O) and a non-polar (CH_2I_2) liquid on the surface of each polymer.

$$1 + cos\theta = 2\sqrt{\gamma_S^D}\left(\frac{\sqrt{\gamma_l^D}}{\gamma_{lv}}\right) + 2\sqrt{\gamma_S^P}\left(\frac{\sqrt{\gamma_l^P}}{\gamma_{lv}}\right) \quad \text{(Equation S5)}$$

γ_S^D and γ_S^P are the dispersion and polar components of the surface free energy of the solid species

γ_l^D and γ_l^P are the dispersion and polar components of the surface free energy of the liquid species

γ_{lv} is the free energy of the liquid species against its saturated vapor

θ is the contact angle (in degrees) of the liquid species against a solid species

The values of γ_l^D, γ_l^P and γ_{lv} were taken from the literature for water (γ_l^D = 21.8 dynes/cm, γ_l^P = 51 dynes/cm, and γ_{lv} = 72.8 dynes/cm) and diiodomethane (γ_l^D=49.5 dynes/cm, γ_l^P = 1.3 dynes/cm, and γ_{lv} = 50.8 dynes/cm).[35] A system of two equations (one equation for each contact angle of each liquid) with two unknowns (γ_S^P and γ_S^D) can then be solved to obtain the values of γ_S^P and γ_S^D for each polymer component. These values were then used in Equation S4 to obtain the respective interfacial tensions.

Table S1: Measured contact angles of water and methylene iodide on various polymer surfaces.

Material	Water contact angle (°)	Methylene iodide contact angle (°)	γ_S (dyne/cm)	γ_S^P (dyne/cm)	γ_S^D (dyne/cm)
PBA	97.1 ± 0.1*	64.5 ± 0.1*	26.0	1.5	24.5
PAC4VG	85.7± 0.1	39.3 ± 0.1	40.1	2.1	38.0
P(S-*co*-BA)	98.5 ± 0.1	40.0 ± 0.1	42.5	0.0	42.5
(P(S-*co*-BA)@PAC4VG	75.1 ± 0.1	50.9 ± 0.1			
PBA@PAC4VG	89.5 ± 0.1	68.2 ± 0.1			

*value taken from Kim *et al.*[40]

Table S2: Interfacial tensions and parameters U and T calculated according to the method of Gonzales-Ortiz.[33]

Polymer	γ_{12}	γ_{1W}	γ_{2W}	T	U

	(dyne/cm)	(dyne/cm)	(dyne/cm)		
P(S-*co*-BA)@PAC4VG	2.3	57.1	48.9	0.82	0.05
PBA@PAC4VG	3.0	46.5	48.9	0.99	0.06

*1=P(S-*co*-BA) or PBA, 2=PAC4VG, W=water

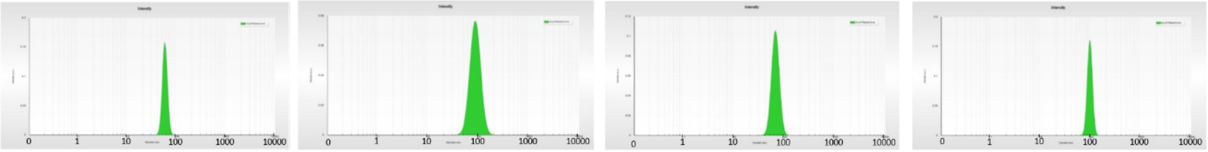

Figure S1: Intensity-average particle hydrodynamic diameters distributions for (from left to right): P(S_{85}-co-BA_{15}), (P(S_{37}-co-BA_6)@PAC4VG$_{57}$, PBA, and PBA$_{30}$@PAC4VG$_{70}$. The subscripts indicate the monomer weight fractions.

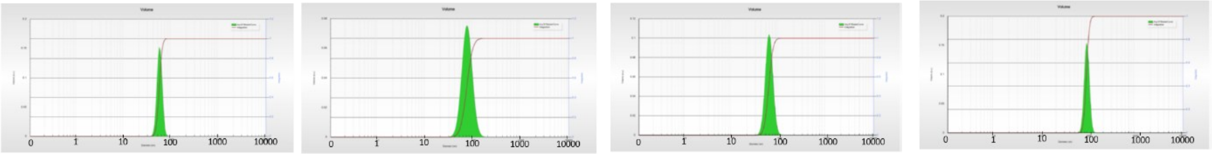

Figure S2: Volume-average particle size distributions for (from left to right): P(S_{85}-co-BA_{15}), (P(S_{37}-co-BA_6)@PAC4VG$_{57}$, PBA, and PBA$_{30}$@PAC4VG$_{70}$. The subscripts indicate the monomer weight fractions.

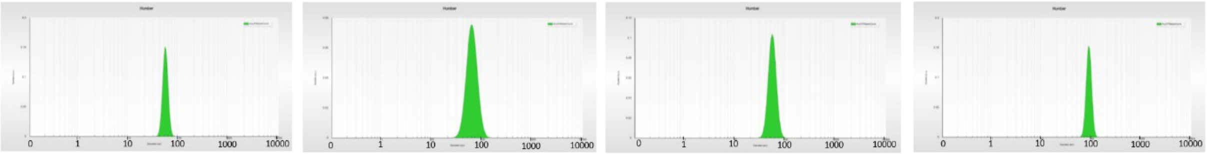

Figure S3: Number-average particle size distributions for (from left to right): P(S_{85}-co-BA_{15}), (P(S_{37}-co-BA_6)@PAC4VG$_{57}$, PBA, and PBA$_{30}$@PAC4VG$_{70}$. The subscripts indicate the monomer weight fractions.

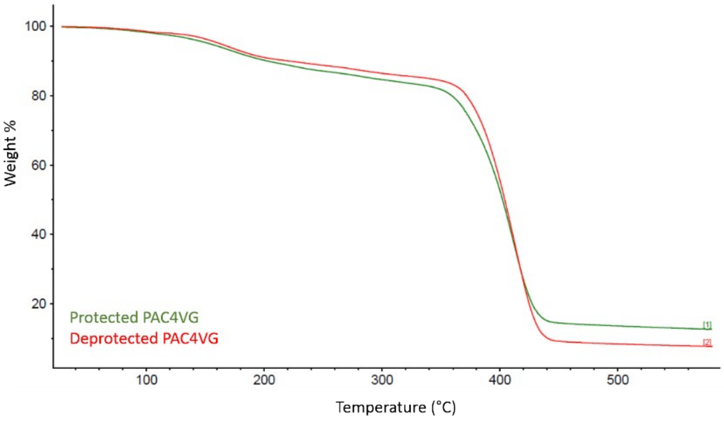

Figure S4: TGA thermograms of protected and deprotected PAC4VG.

Estimation of a copolymer T_g based on the T_g of the pure components using the Fox-Flory equation:

$$\frac{1}{T_{g,copolymer}} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \qquad \text{(Equation S6)}$$

where,

w_1 and w_2 are the weight fractions of polymers 1 and 2

$T_{g,1}$ and $T_{g,2}$ are the individual glass transition temperatures of polymers 1 and 2 (in Kelvin)

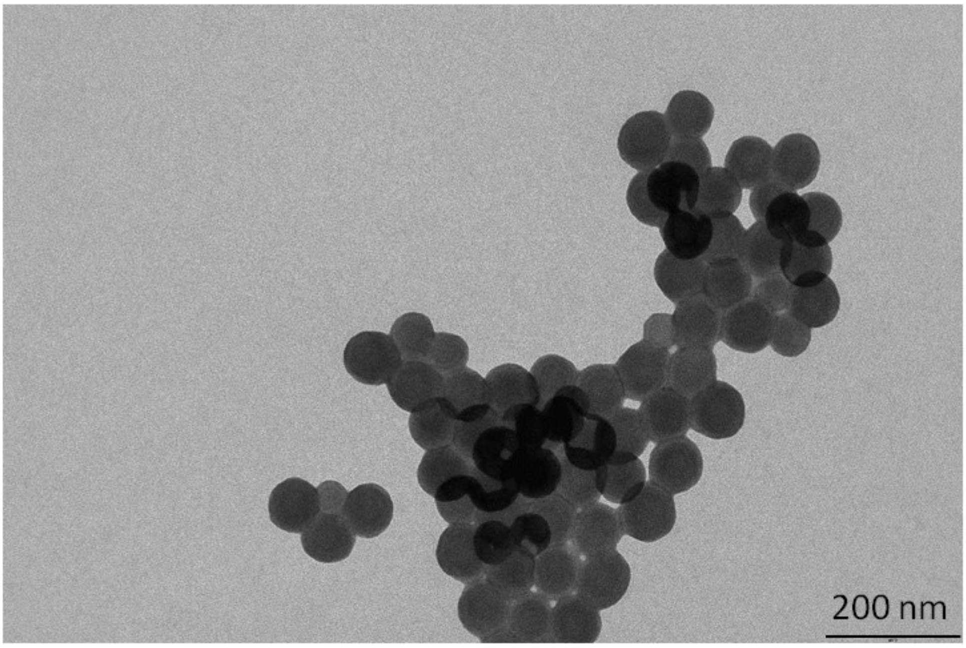

Figure S5 : TEM image of P(S-co-BA)@PAC4VG latex particles.

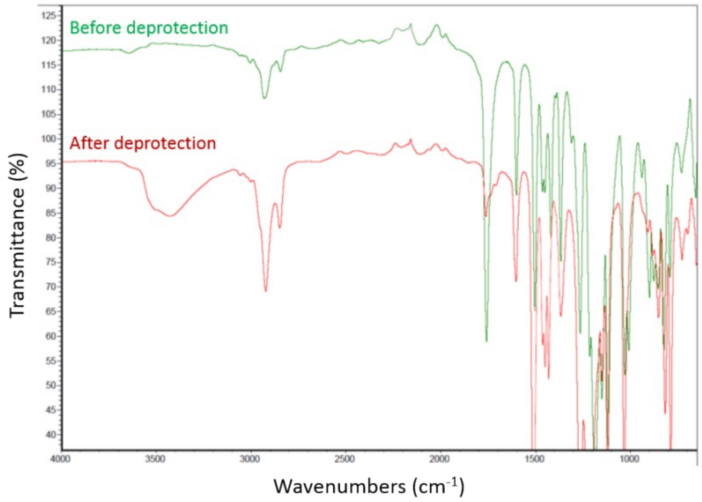

Figure S6: FTIR analysis of PAC4VG before and after deprotection.

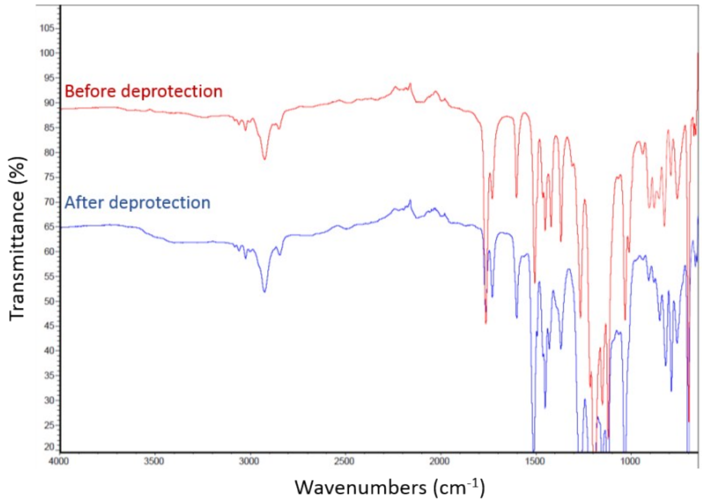

*Figure S7: FTIR analysis of P(S-*co*-BA)@PAC4VG before and after deprotection.*

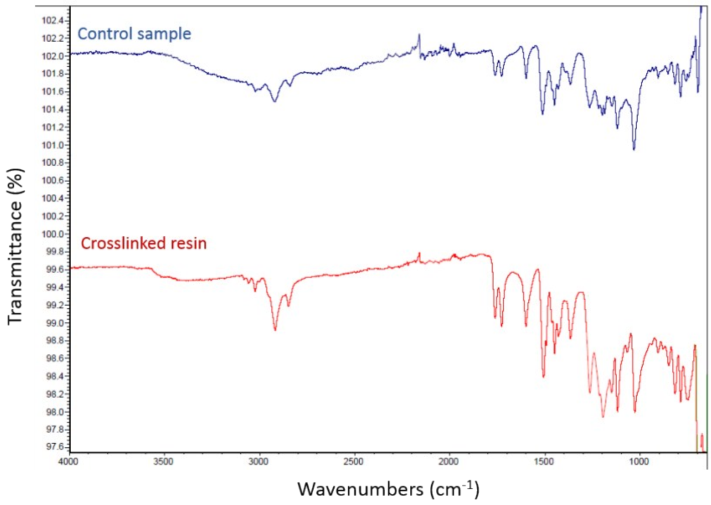

Figure S8: FTIR analysis of control sample (non-crosslinked) and crosslinked resin.