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Supporting Information

Biobased homopolymers and amphiphilic diblock copolymers containing guaiacyl (G) or hydroxyphenyl (H) lignin derivatives synthesized by RAFT (PISA)

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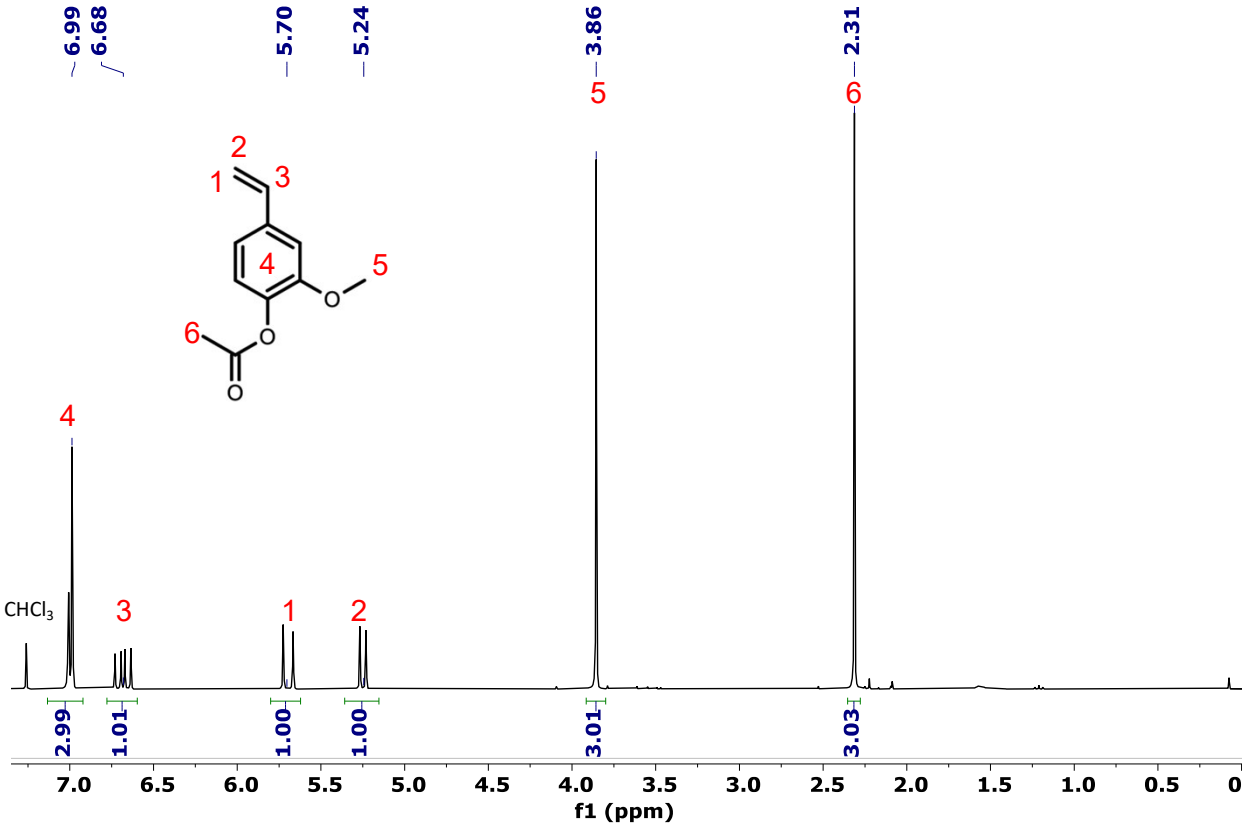


Figure S1. ^{1}H NMR spectrum of AcVG recorded in $CDCl_3$.

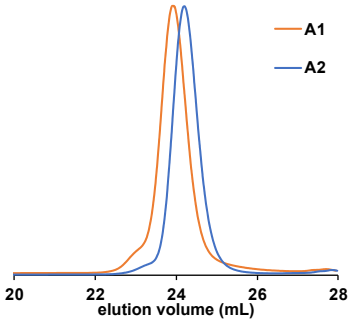


Figure S2. Normalized size exclusion chromatograms (RI) in THF of samples A1 (PAcVG) and A2 (PAcST).

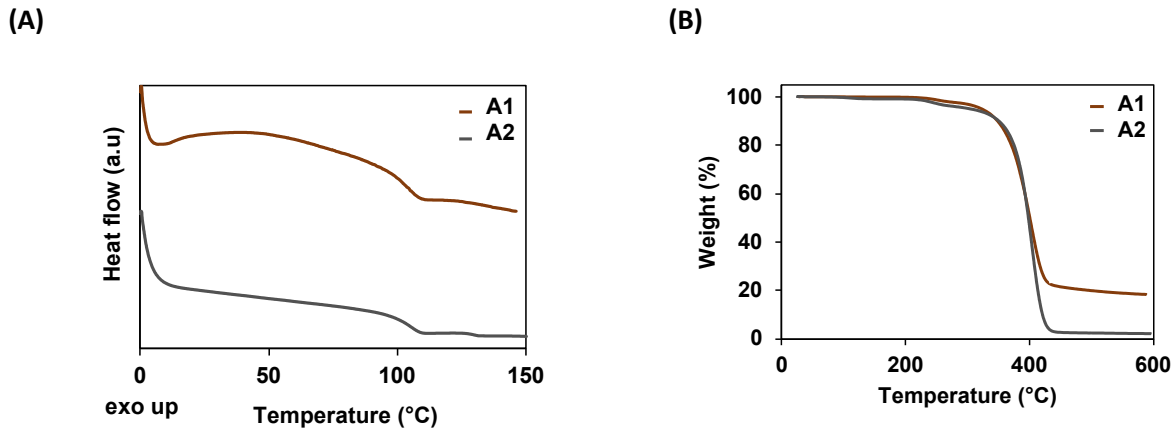
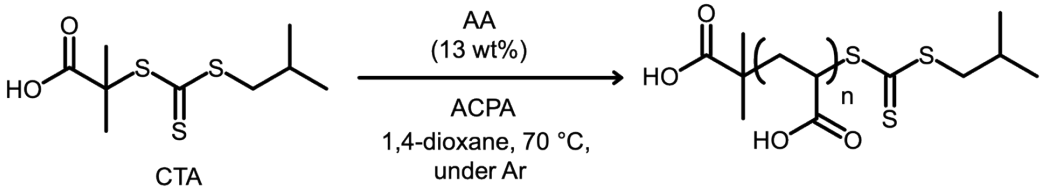


Figure S3. (A) DSC thermograms obtained during the 2nd heating under N_2 with a heating rate of 20 °C.min^{-1} of: A1 (PAcVG) and A2 (PAcST). B). TGA thermograms obtained under N_2 with a heating rate of 20 °C.min^{-1} of A1 (PAcVG) and A2 (PAcST).



Scheme S1. RAFT polymerization of acrylic acid.

Table S1. Experimental conditions for the synthesis of PAA homopolymers in the presence of CTA and their characteristics[#]

Sample	$[AA]_0/[CTA]_0$	Time (h)	Conv.[a] (%)	$M_{n,th}$[b] (kg/mol)	$DP_{n,NMR}$[c]	$M_{n,NMR}$[c] (kg/mol)	$M_{n,SEC}$[d] (kg/mol)	$Đ$[d]
M1	57/1	4	85	3.8	50	4.0	4.5	1.12
M2	30/1	3	87	2.1	25	2.1	3.1	1.09

"[#]Polymerizations were performed in 1,4-dioxane at 70 °C in presence of the RAFT agent CTA and ACPA as a radical initiator at 13 wt% of monomer at an initial molar ratio of CTA/ACPA: 1/0.1. [a] Determined by ^{1}H NMR analysis. [b] Determined from final conversion. [c] Determined by ^{1}H NMR analysis in DMSO_d_6 from end-chain. [d] Determined by SEC in THF for the methylated polymers with a PS calibration and recalculated for the nonmethylated ones.

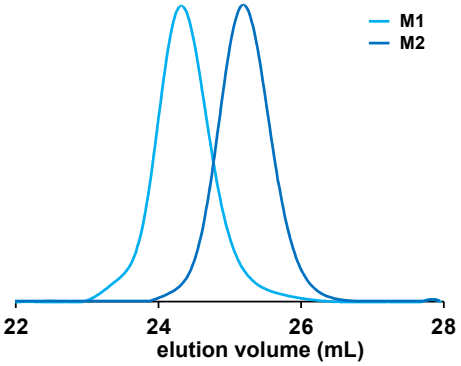


Figure S4. Normalized size exclusion chromatograms (RI) in THF of methylated samples M1 (PAA_{50}-TTC) and M2 (PAA_{25}-TTC).

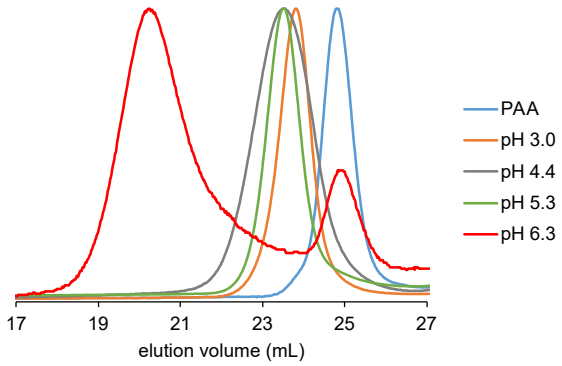


Figure S5. Normalized size exclusion chromatograms (RI) in THF of methylated PAA_{50}-TTC (M1) and PAA-*b*-PAcVG obtained by PISA *via* aqueous RAFT emulsion polymerization at pH 3 (B1), 4.4 (B2), 5.3 (B3) and 6.3 (B4).

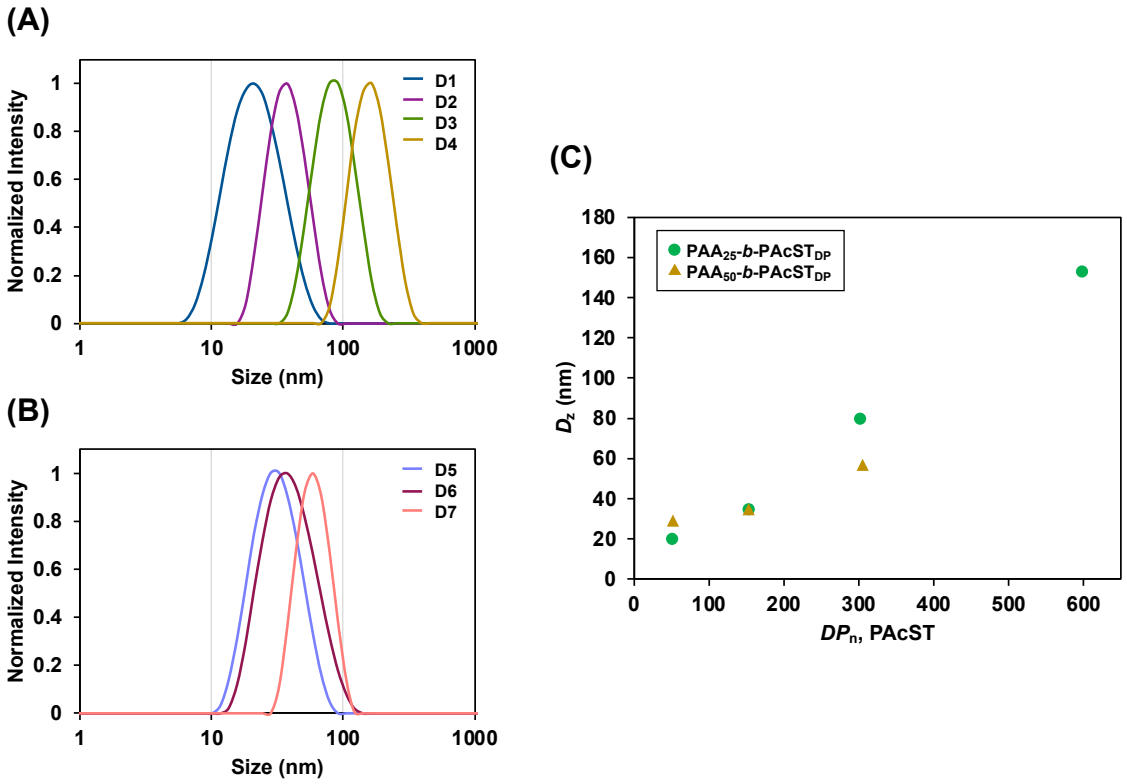


Figure S6. DLS distributions by intensity of (A) D1, D2, D3, D4 (B) D5, D6 and D7 latexes diluted at 1 wt%. (C) Z-average particle diameter (D_z) as a function the hydrophobic block length, $DP_{n,\ PAcST}$ from PAA_{25}-TTC (M2) (circle) and PAA_{50}-TTC (M1) (triangle).

(A) (B)

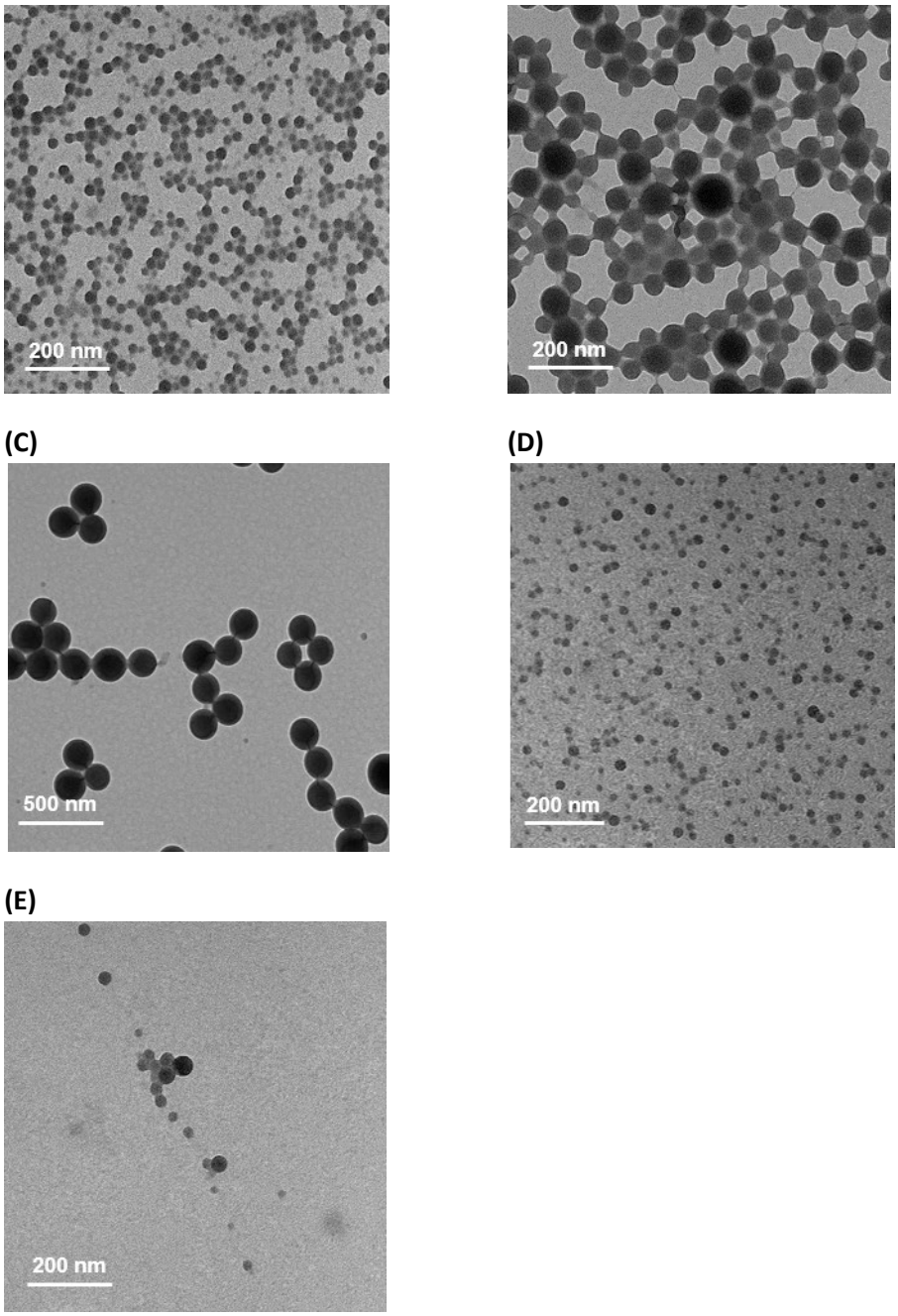
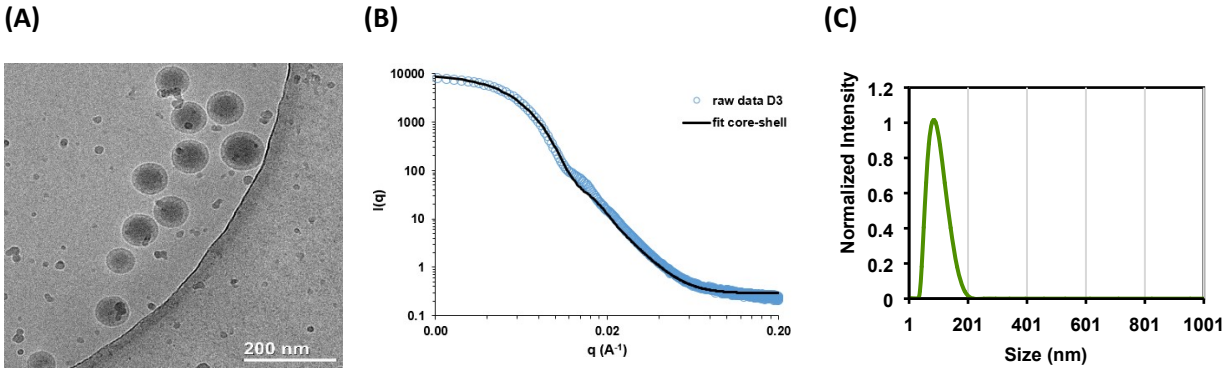


Figure S7. Representative TEM images prepared at room temperature for samples D2 (A), D3 (B), D4 (C), D6 (D) and D7 (E) from latexes diluted at 0.2 wt%.



D_n = 75 nm

SD = 6 nm

D_c = 63 nm

PDI = 0.2

t = 2.5 nm

PDI = 0.1

D_z = 80 nm

PDI = 0.09

Figure S8. (A) Representative cryo-TEM image of sample D3 (diluted at 1 wt%) with D_n, the number-average diameter determined on 20 representative nano-objects and SD, the standard deviation. (B) SAXS profiles of *sample D3* (diluted 1 wt%) with D_c, the core diameter and t, the shell thickness using a sphere core-shell model and a lognormal distribution. (C) Normalized size distribution determined by DLS at 1 wt% in water for dispersion D3 with D_z, the Z-average particle diameter. PDI = polydispersity index.

Determination of the blocking efficiency

The weight fraction of the residual methylated macro-RAFT agent in the methylated polymer was calculated from the RI peak area of the methylated macro-RAFT agent remaining unreacted during polymerization obtained by size exclusion chromatography with the online RI detector as follows:

$$\mathbf{F_{residual\ macro\text{-}RAFT\ agent} = RI\ area_{\ residual\ macro\text{-}RAFT\ agent} * n_0 / (C_{polym.} * \mathit{dn/dC} * V_{inj.} * K_{RI})}$$

With

$n_0 = 1.405$, the refractive index of THF

$K_{RI} = 1.58*10^6$, the refractometer constant (mV)

dn/dC = 0.067[1], the refractive index increment of methylated PAA ($mL.g^{-1}$)

$C_{polym} = 5$, the methylated polymer solution concentration ($mg.mL^{-1}$)

$V_{inj.} = 0.1$, the injection volume of the polymer solution (mL)

Note: In the RI chromatograms, the final copolymer peak overlapped with the unreacted macro-RAFT agent peak (Figures 3 and 5 in the main manuscript). Therefore, deconvolution of SEC data was necessary to determine the area of each RI peak. We used a method previously described in the literature.[1] Figure S9 shows an example of results obtained after deconvolution process (sample C5).

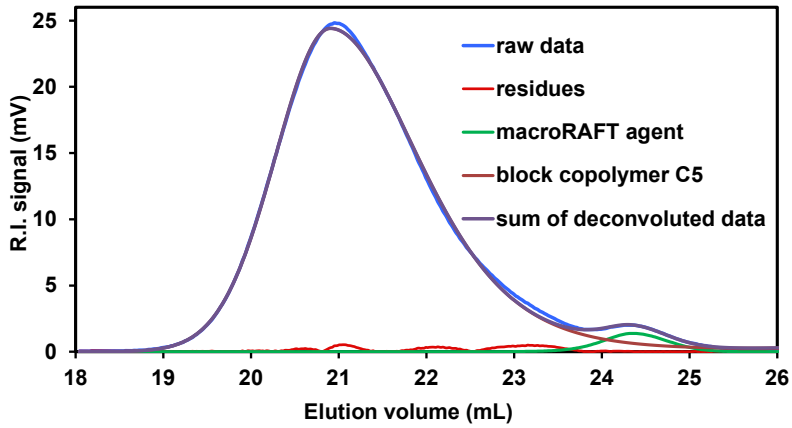


Figure S9. Result of deconvolution with an exponentially modified Gaussian model (Sample C5, Table 3).

The following equation has been used for the calculation of the blocking efficiency:

$$\mathbf{Blocking\ efficiency\ (\%) = (1- F_{residual\ macro\text{-}RAFT\ agent} / F_{macro\text{-}RAFT\ agent}) *100}$$

With

$F_{macro\text{-}RAFT\ agent}$, the weight fraction of methylated macro-RAFT agent in the methylated polymer.

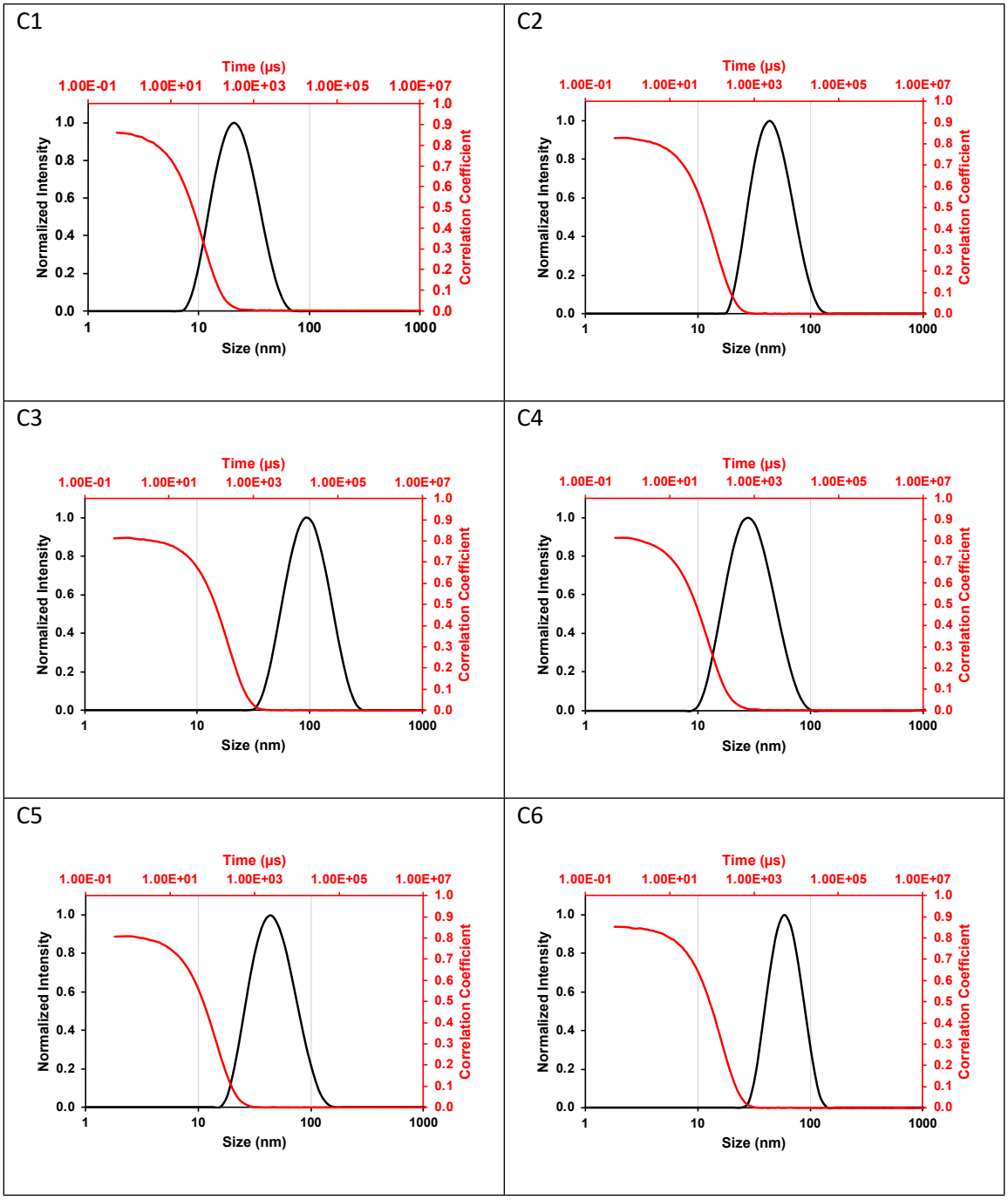
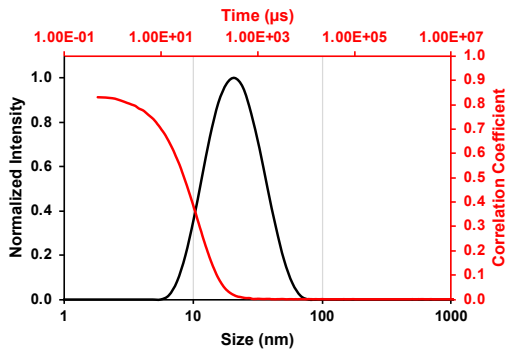
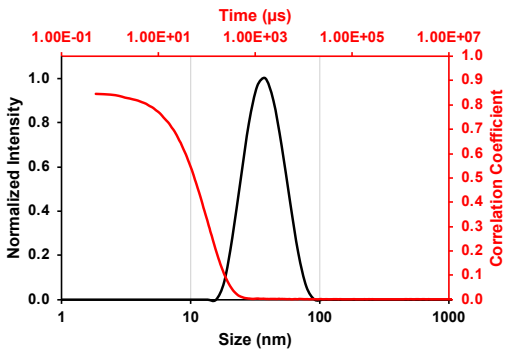


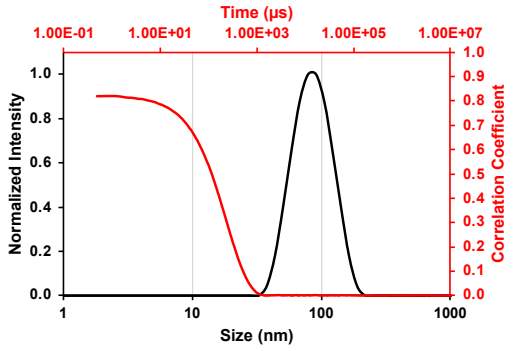
Figure S10. Normalized size distributions and correlograms obtained by DLS at 1 wt% in water for dispersions C1 to C6 (Table 3).

D1	D2

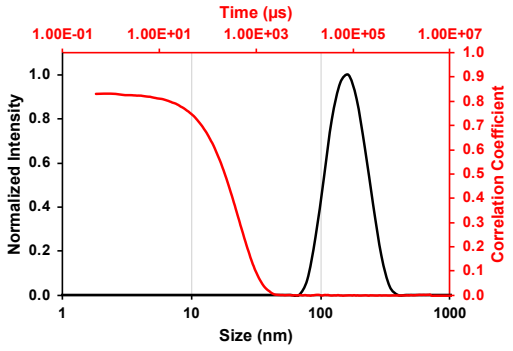

Time (µs)
1.00E-01
1.00E+01
1.00E+03
1.00E+05
1.00E+07
Normalized Intensity
Correlation Coefficient
Size (nm)
1
10
100
1000


Time (µs)
1.00E-01
1.00E+01
1.00E+03
1.00E+05
1.00E+07
Normalized Intensity
Correlation Coefficient
Size (nm)
1
10
100
1000

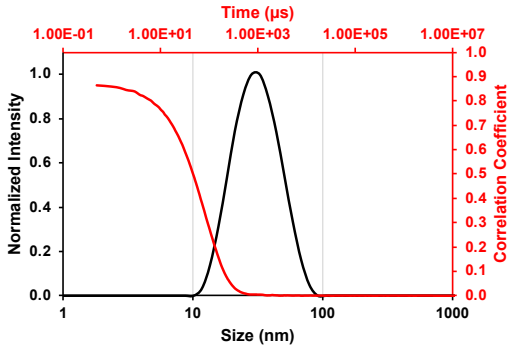
D3


Time (µs)
1.00E-01
1.00E+01
1.00E+03
1.00E+05
1.00E+07
Normalized Intensity
Correlation Coefficient
Size (nm)
1
10
100
1000

D4


Time (µs)
1.00E-01
1.00E+01
1.00E+03
1.00E+05
1.00E+07
Normalized Intensity
Correlation Coefficient
Size (nm)
1
10
100
1000

D5


Time (µs)
1.00E-01
1.00E+01
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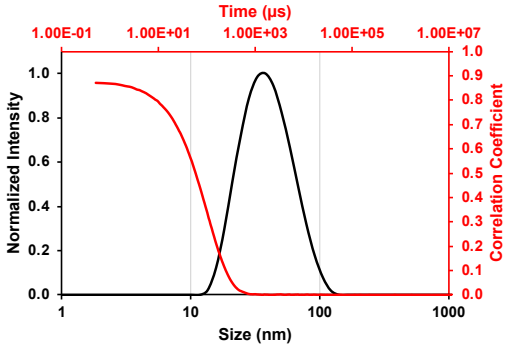
1.00E+07
Normalized Intensity
Correlation Coefficient
Size (nm)
1
10
100
1000

D6


Time (µs)
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1.00E+01
1.00E+03
1.00E+05
1.00E+07
Normalized Intensity
Correlation Coefficient
Size (nm)
1
10
100
1000

D7

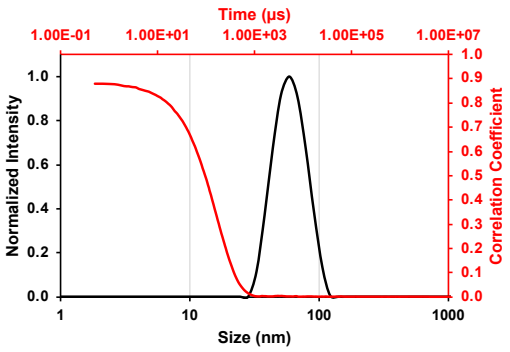

Figure S11. Normalized size distributions and correlograms obtained by DLS at 1 wt% in water for dispersions D1 to D7 (Table 4).

Reference

[1] E. Velasquez, G. Pembouong, J. Rieger, F. Stoffelbach, O. Boyron, B. Charleux, F. D'Agosto, M. Lansalot, P.-E. Dufils and J. Vinas, *Macromolecules*, 2013, 46, 664.