Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Supporting Information

Detection of coalescing agents in water borne latex emulsions using an environment sensitive fluorescent probe

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Emulsion Polymerization recipe

Table S1. Emulsion polymerization recipe for the preparation of labeled and non-labeled low and high T_g styrene-co-ethylhexylacrylate (S/2-EHA) latices.

	Non-labeled		Labeled	
Component weight (g)	S/2-EHA20	S/2-EHA60	S/2-EHA20	S/2-EHA60
Water	885	885	885	885
Sodium laurylsulphate (SLS)	19.704	19.704	19.704	19.704
ammonium phosphate (AP)	1.77	1.77	1.77	1.77
MFT (1) fluorescent probe	0	0	0.012	0.012
acrylic acid	11.823	11.823	11.823	11.823
Styrene	339.128	473.505	339.128	473.505
2-ethylhexylacrylate	240.183	105.794	240.183	105.794
isoascorbic acid 5%	0.60	0.60	0.60	0.60
tert-butyl hydroxyperoxide (t-BHPO)	0.84	0.84	0.84	0.84
Proxel ultra 10	1.5	1.5	1.5	1.5

Table S2. Emulsion polymerization recipe for the preparation of labeled and non-labeled low and high T_g methyl methacrylate-co-ethylacrylate (MMA/EA) latices.

	Non-labeled		Labeled	
Component weight (g)	MMA/EA20	MMA/EA60	MMA/EA20	MMA/EA60
Water	885	885	885	885
Sodium laurylsulphate (SLS)	19.704	19.704	19.704	19.704
ammonium phosphate (AP)	1.77	1.77	1.77	1.77
MFT (1) fluorescent probe	0	0	0.012	0.012
acrylic acid	11.82	11.82	11.82	11.82
methyl methacrylate (MMA)	248.292	425.11	248.292	425.11
ethylacrylate (EA)	331.007	154.189	331.007	154.189
isoascorbic acid 5%	0.60	0.60	0.60	0.60
tert-butyl hydroxyperoxide (t-BHPO)	0.84	0.84	0.84	0.84
Proxel ultra 10	1.5	1.5	1.5	1.5

Physical Characteristics of Coalescing Agents

Table S3. Physical properties of the five coalescing agents used in present research work.

Coalescing agent	Mol. Wt. (g/mol)	Water solubility (%)	Viscosity (mPa s)	Surface tension (dynes/cm)	bp (ºC)
EEH	174.3	0.2	7.0	27.6	224
Texanol	216.3	2		28.9	244
DPnB	190.3	5	4.4	28.8	229
EEA	132.2	24	1.3	28.2	150
DPM	148.2	100	3.4	29	188

Steady-State Fluorescence Data of Latices

Table S4. Fluorescence emission λ_{max} of hydrophobic S/2-EHA latices formulated with the five coalescing agents.

	Emission maximum (nm)				
%w/w	EEH	Texanol	DPnB	EEA	DPM
		S/2-EHA20			
0	453	449	449	449	
3	459	456	455	455	
6	466	463	462	461	
9	472	470	468	469	
		S/2-EHA60			
0	449	448	448	445	448
3	454	452	453	451	449
6	458	456	455	455	450
9	462	460	460	460	450

Table S5. Fluorescence emission λ_{max} of hydrophilic MMA/EA latices formulated with the five coalescing agents.

	Emission maximum (nm)				
%w/w	EEH	Texanol	DPnB	EEA	DPM
		MMA/EA20			
0	479	477	477	478	477
3	485	482	485	484	479
6	493	489	493	493	480
9	499	495	499	501	481
		MMA/EA60			
0	469	468	468	469	468
3	473	469	471	472	469
6	479	474	478	477	470
9	484	479	486	484	470

Steady-State fluorescence band shape parameters

Table S6. Fluorescence band shape parameters of S/2-EHA T_g 20 °C latex, values obtained after fitting steady-state data with equation 1.

		S/2-EHA T_g 20 °C		
Co-solvent % w/w	Emission max. (nm)	Intensity (a.u.)	Width (nm)	Skew
EEH 0%	452.6	3.52×10^{08}	105	0.35
EEH 3%	458.8	3.39×10^{08}	114	0.42
EEH 6%	466.4	2.97×10^{08}	115	0.36
EEH 9%	471.9	2.66×10^{08}	124	0.37
Texanol 0%	449.4	1.18×10^{06}	82	0.42
Texanol 3%	456.1	9.35×10^{05}	88	0.39
Texanol 6%	462.6	8.24×10^{05}	95	0.37
Texanol 9%	469.9	7.35×10^{05}	100	0.36
DPnB 0%	449.4	5.62×10^{04}	81	0.42
DPnB 3%	455.4	4.80×10^{04}	87	0.40
DPnB 6%	462.1	4.18×10^{04}	93	0.38
DPnB 9%	467.9	3.76×10^{04}	99	0.36
EEA 0%	448.7	1.59×10^{08}	81	0.40
EEA 3%	454.7	1.32×10^{08}	87	0.38
EEA 6%	460.9	1.16×10^{08}	93	0.37
EEA 9%	468.6	1.05×10^{08}	100	0.34
DPM 0%	441.6	4.23×10^{08}	95	0.43
DPM 3%	441.9	1.48×10^{08}	86	0.48
DPM 6%	442.6	1.99×10^{08}	87	0.50
DPM 9%	441.6	1.32×10^{07}	80	0.49

Table S7. Fluorescence parameters of S/2-EHA T_g 60 °C latex, obtained after fitting band shapes with equation 1.

	S/2-EHA T_g 60 °C			
Co-solvent % w/w	Emission max. (nm)	Intensity (a.u.)	Width (nm)	Skew
EEH 0%	448.7	2.84×10^{08}	100	0.42
EEH 3%	454.1	2.73×10^{08}	107	0.37
EEH 6%	458.4	2.59×10^{08}	112	0.35
EEH 9%	461.7	2.40×10^{08}	117	0.40
Texanol 0%	447.6	4.47×10^{05}	82	0.43
Texanol 3%	452.2	4.66×10^{05}	88	0.41
Texanol 6%	456.3	4.45×10^{05}	93	0.39
Texanol 9%	460.4	4.24×10^{05}	98	0.38
DPnB 0%	447.6	4.47×10^{05}	82	0.43
DPnB 3%	452.8	4.45×10^{05}	89	0.40
DPnB 6%	455.4	4.45×10^{05}	92	0.40
DPnB 9%	460.2	4.0×10^{05}	98	0.38
EEA 0%	445.5	1.19×10^{08}	83	0.45
EEA 3%	451.0	1.02×10^{08}	88	0.42
EEA 6%	454.9	1.01×10^{08}	91	0.40
EEA 9%	460.2	9.37×10^{07}	97	0.36
DPM 0%	447.6	4.47×10^{05}	82	0.43
DPM 3%	449.2	4.47×10^{05}	86	0.44
DPM 6%	449.9	4.43×10^{05}	87	0.43
DPM 9%	450.2	4.38×10^{05}	87	0.43

Table S8. Fluorescence parameters of MMA/EA T_g 20 °C latex, obtained after fitting band shapes with equation 1.

		MMA/EA T_g 20 °C		
Co-solvent % w/w	Emission max. (nm)	Intensity (a.u.)	Width (nm)	Skew
EEH 0%	478.6	2.92×10^{08}	120	0.33
EEH 3%	485.0	2.52×10^{08}	126	0.35
EEH 6%	493.4	2.09×10^{08}	130	0.32
EEH 9%	498.7	1.20×10^{08}	136	0.31
Texanol 0%	477.0	4.79×10^{05}	101	0.32
Texanol 3%	482.2	3.91×10^{05}	106	0.31
Texanol 6%	489.2	3.32×10^{05}	111	0.31
Texanol 9%	494.9	2.69×10^{05}	115	0.30
DPnB 0%	477.0	4.79×10^{05}	101	0.32
DPnB 3%	484.6	3.54×10^{05}	107	0.31
DPnB 6%	492.7	2.99×10^{05}	113	0.30
DPnB 9%	499.3	2.49×10^{05}	119	0.29
EEA 0%	478.0	3.41×10^{08}	127	0.35
EEA 3%	484.3	2.61×10^{08}	125	0.34
EEA 6%	492.9	2.23×10^{08}	127	0.33
EEA 9%	500.8	1.92×10^{08}	132	0.31
DPM 0%	477.0	4.79×10^{05}	101	0.32
DPM 3%	478.6	4.23×10^{05}	103	0.32
DPM 6%	479.8	3.95×10^{05}	104	0.32
DPM 9%	481.2	3.76×10^{05}	105	0.32

Table S9. Fluorescence parameters of MMA/EA T_g 60 °C latex, obtained after fitting band shapes with equation 1.

	MMA/EA T_g 60 °C			
Co-solvent % w/w	Emission max. (nm)	Intensity (a.u.)	Width (nm)	Skew
EEH 0%	468.7	3.03×10^{08}	118	0.37
EEH 3%	472.7	3.00×10^{08}	118	0.35
EEH 6%	479.2	2.84×10^{08}	125	0.37
EEH 9%	484.3	2.43×10^{08}	128	0.36
Texanol 0%	468.2	4.97×10^{05}	97	0.34
Texanol 3%	469.3	5.18×10^{05}	98	0.34
Texanol 6%	474.0	4.73×10^{05}	101	0.34
Texanol 9%	479.0	4.18×10^{05}	105	0.33
DPnB 0%	468.2	4.97×10^{05}	97	0.34
DPnB 3%	470.7	4.53×10^{05}	99	0.34
DPnB 6%	478.0	4.39×10^{05}	104	0.33
DPnB 9%	485.7	3.21×10^{05}	111	0.33
EEA 0%	468.8	3.55×10^{08}	123	0.37
EEA 3%	471.6	3.09×10^{08}	115	0.35
EEA 6%	477.1	3.01×10^{08}	123	0.36
EEA 9%	484.2	2.85×10^{08}	127	0.35
DPM 0%	468.2	4.97×10^{05}	97	0.34
DPM 3%	469.1	4.68×10^{05}	97	0.34
DPM 6%	469.7	4.68×10^{05}	98	0.34
DPM 9%	470.4	4.53×10^{05}	99	0.34

Gel permeation chromatography of MFT-copolymerized S/2-EHA and MMA/EA latices

The distribution of copolymerized MFT in the copolymer in S/2-EHA and MMA/EA latices was analyzed with gel permeation chromatography (GPC) using a Waters Alliance Gel Permeation Chromatograph coupled with a Waters 410 dRI refractive index detector and a Shimadzu RF 10a XL fluorescence detector (excitation 380 nm; detection 570 nm). Tetrahydrofuran (THF; stabilized HPLC grade, 99.8% pure) containing 1% acetic acid at a flow rate of 1.0 ml/min was used as eluent. One guard column PLgel 10 µm (50 × 7.5 mm) and three PLgel 10 µm Mixed-B (300 × 7.5 mm) columns were used. Polymer standards were Polystyrene MP 160-10 000 000.

GPC traces of S/2-EHA and MMA/EA T_g 20 and 60 ℃ latices are presented in fig. S1. Neat latices were also measured and they showed no fluorescent signal at this retention time. It is quite obvious from fig. S1 that the peaks of refractive index and fluorescence emission emerge at the same retention time. This shows that MFT is homogeneously distributed over the whole molecular weight range of the copolymer.

The fluorescence signal for MMA/EA T_g 20 ℃ (fig. S1c) was weaker than the other three due to a lower amount of copolymerized MFT (6 ppm vs. 18 ppm).

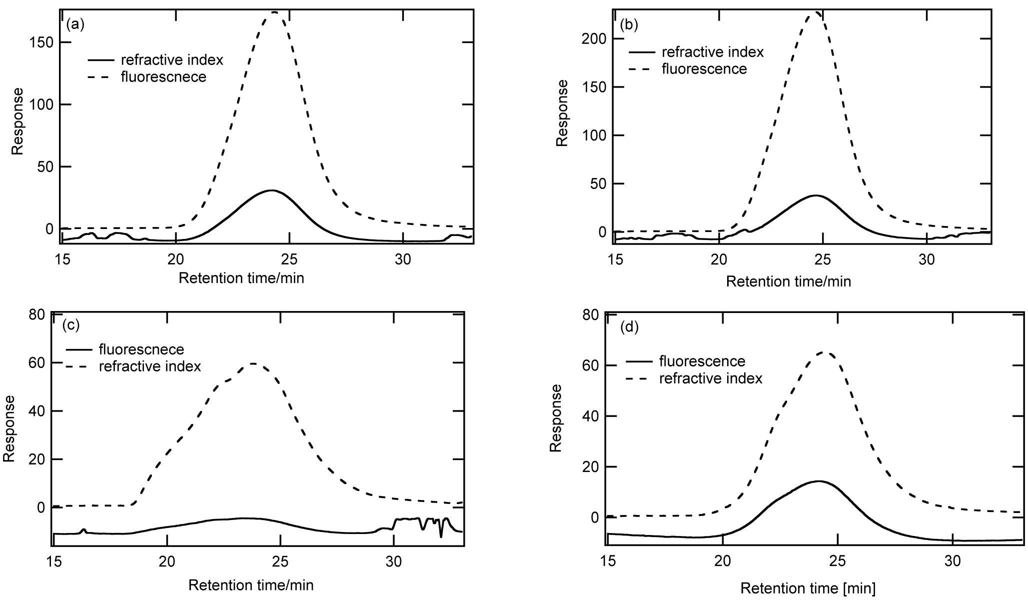

Fig. S1. GPC chromatograms showing refractive index and fluorescence signals of (a) S2-EHA T_g 20 ℃, (b) S/2-EHA T_g 60 ℃, (c) MMA/EA T_g 20 ℃, (d) MMA/EA T_g 60 ℃.

Time-Resolved fluorescence of neat hydrophobic S/2-EHA latex (non-labeled latex)

Blank samples of S/2-EHA low and high T_g non-labeled and non-formulated latices were measured on TCSPC (fig. S2). It is worth to mention that both of these unlabeled latices exhibited decay in the region of interest, i.e. 400-600 nm with two lifetimes; longer lifetime (small amplitude) and shorter lifetime (larger amplitude) showing that latex contained some impurity. For low T_g neat (non-labeled) latex at 440 nm wavelength time components were; τ_0 2.9 ns (A_0 30%) and shorter τ_1 0.5 ns (A_1 70%). For high T_g latex it was τ_0 7.2 ns (A_0 48%) and shorter time component τ_1 1.4 ns (A_1 50%) showing that while measuring labeled latices at this particular wavelength fluorescence decay could have an inaccuracy due to lifetime component impurities present in the latex. Due to this impurity it can be expected that values of lifetime of labeled latex at λ_{max} = 440 nm would be slightly higher than the actual.

(a) (b)

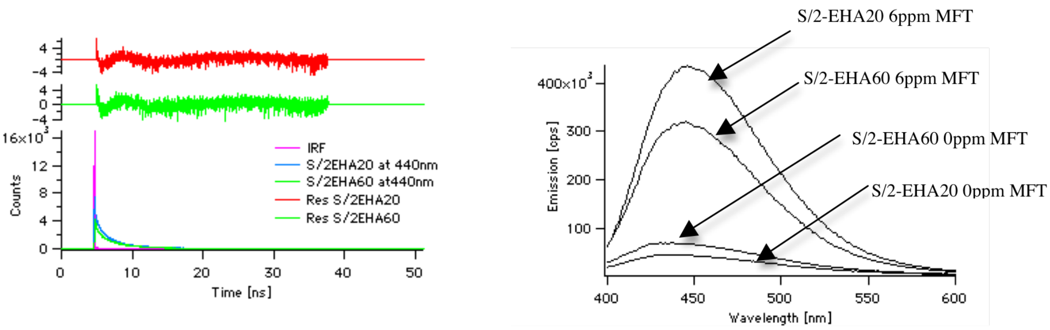

Fig. S2. Fluorescence decay of S/2-EHA T_g 20 and 60 °C blank samples (no fluorescent probe, no co-solvent), (a) time-resolved fluorescence (λ_{exc} = 375 nm measured at 440 nm wavelength) (b) steady-state fluorescence (λ_{exc} = 380nm)

Time resolved of hydrophilic MMA/EA neat latex (non-labeled latex)

Like styrene-based latex, MMA/EA low and high T_g non-labeled and non-formulated latices also exhibited bi-exponential decay due to impurity. Low T_g MMA/EA latex exhibited two lifetimes τ_0 4-6 ns (A_0 27-36%) and τ_1 1 ns (A_1 72-63%). High T_g MMA/EA latex showed τ_0 3.8-6 ns (A_0 37-31%) and τ_1 1 ns (A_1 62-68%).