Supporting Information

Novel Synthesis of Multi-Scaled, Surfactant-Free Monodisperse Latexes via Dispersion Polymerization in a Mixed Ionic/Non-ionic Initiator System

I-Chen Chou[1], Wen-Yen Chiu[*,1,2,3]

[1]Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan
[2]Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan
[3]Department of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan

Tel: +886-2-23623259

Fax: +886-2-23623259

E-mail: ycchiu@ntu.edu.tw

Table S1. The decomposition rate constants of the initiators employed into the latex synthesis[a]

Initiator	Type	k_d (S^{-1})	Condition	10h half-life ^oC (Solvent)
VA-044	Catonic	4.83×10^{-5}	Methanol/50 ^oC	44 (Water)
		4.02×10^{-5}	Water/50 ^oC	
AIBA	Catonic	1.52×10^{-4}	Water/70 ^oC	56 (Water)
KPS[b]	Anionic	6.89×10^{-5}	Water/80 ^oC	60 (Water)
				70 (0.1M NaOH)
ADVN	Non-ionic	1.98×10^{-4}	Toluene/70 ^oC	51 (Toluene)
AIBN	Non-ionic	4.03×10^{-5}	Toluene/70 ^oC	65 (Toluene)
ACHN	Non-ionic	6.50×10^{-6}	Toluene/80 ^oC	88 (Toluene)

a. The experimental results showed that colloidal stable latexes can still be obtained if the $\boldsymbol{k_d}$ of the ionic initiator is on the same order even a little bit smaller than the $\boldsymbol{k_d}$ for non-ionic initiator, such as the combination of AIBA/ADVN pair. However, the monodispersity would gradually decrease as using ionic initiator with smaller $\boldsymbol{k_d}$. This is attributed to the fact that new latex particles were generated till high monomer conversion.

b. Persulfate decomposition is pH dependent.

Table S2. The recipe for dispersion polymerization of styrene in solely AIBA initiation system [a]

Sample code	Methanol/Water (ml)	AIBA(g)	Reaction Temperature(^{o}C)	Stirring Rate(rpm)	d_n(μm)[b]	CV(%)	M_w(/10^4) (g/mol)
A-PS1	50/0	0.025	60	100	0.97	6.2	72.86
A-PS2	100/0	0.025	60	100	0.42	>50	74.06
A-PS3	25/0	0.025	60	100	1.42	4.8	68.64
A-PS4	100/0	0.025	60	300	0.57	>50	61.63
A-PS5	50/0	0.025	45	100	1.06	5.3	150.70
A-PS6	50/0	0.1	60	100	/[c]	/	31.67
A-PS7	45/5	0.025	60	100	0.51	2.5	70.50
A-PS8	40/10	0.025	60	100	0.38	7.6	34.80
A-PS9	40/10	0.025	45	100	0.5	2.3	153.40

[a] Conditions: 5g styrene monomer. AIBA: 2,2'-Azobis(2-methylpropionamide) dihydrochloride. [b] Average diameter by counting 150 latexes. [c] Non-spherical particles.

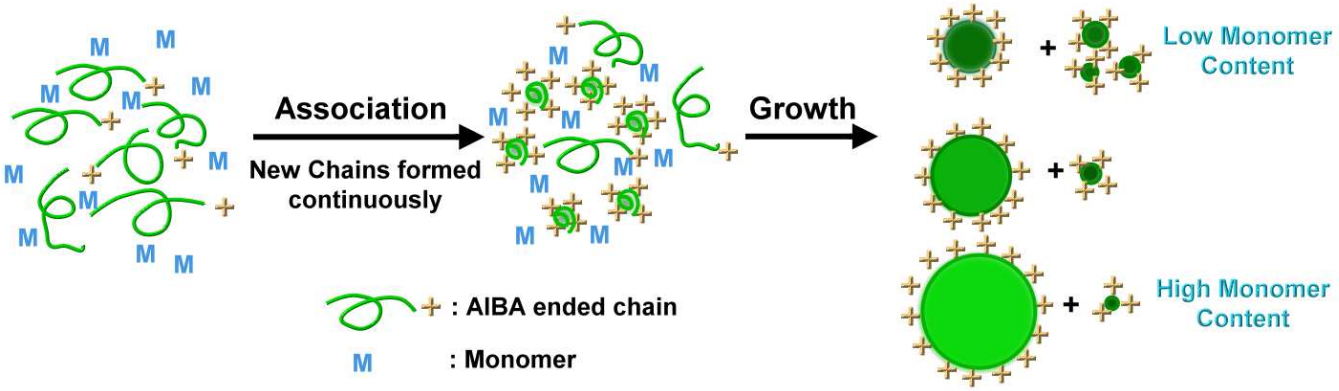


Figure S1. A schematic representation of particle formation and growth in soap-free alcoholic dispersion polymerization in solely AIBA initiation system.

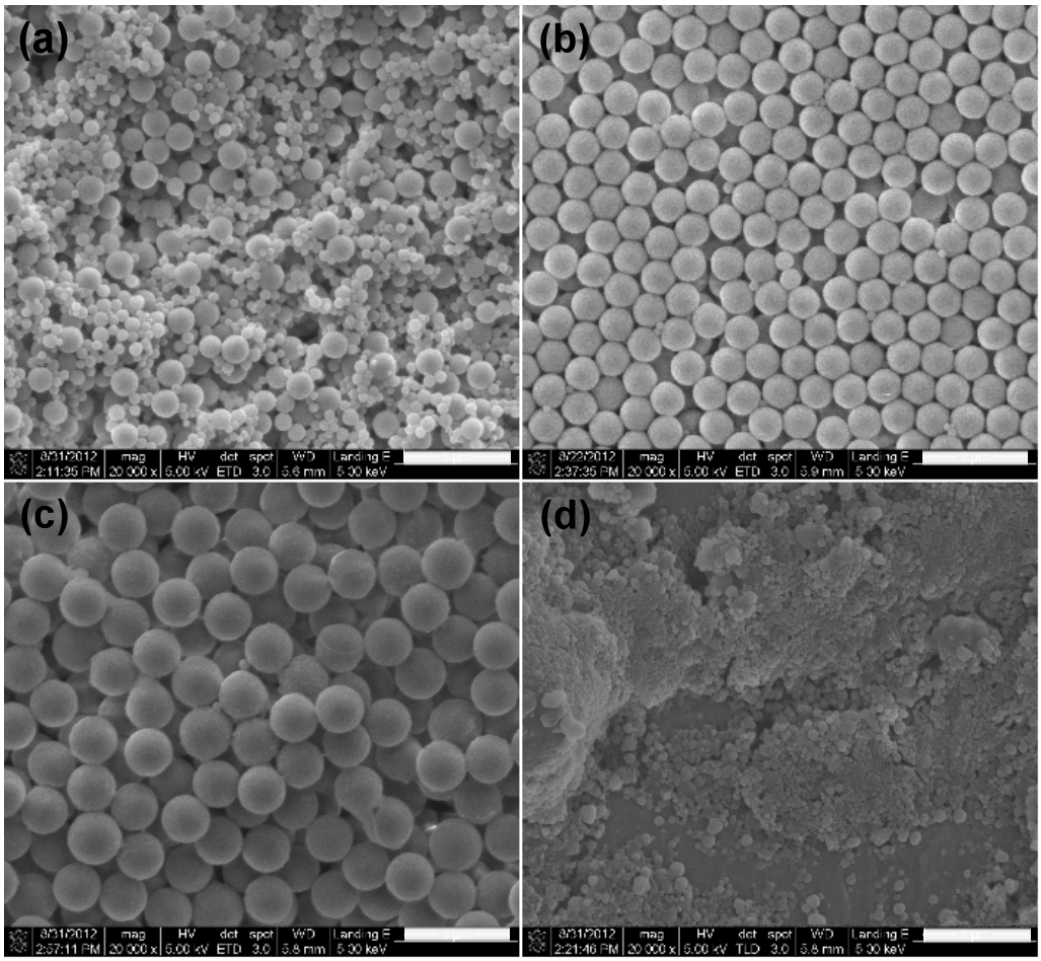


Figure S2. Representative SEM images of AIBA-PS latexes synthesized in pure methanol via dispersion polymerization. Scale bar: 3μm. (a)A-PS2 (b)A-PS1 (c)A-PS3 (d)A-PS6

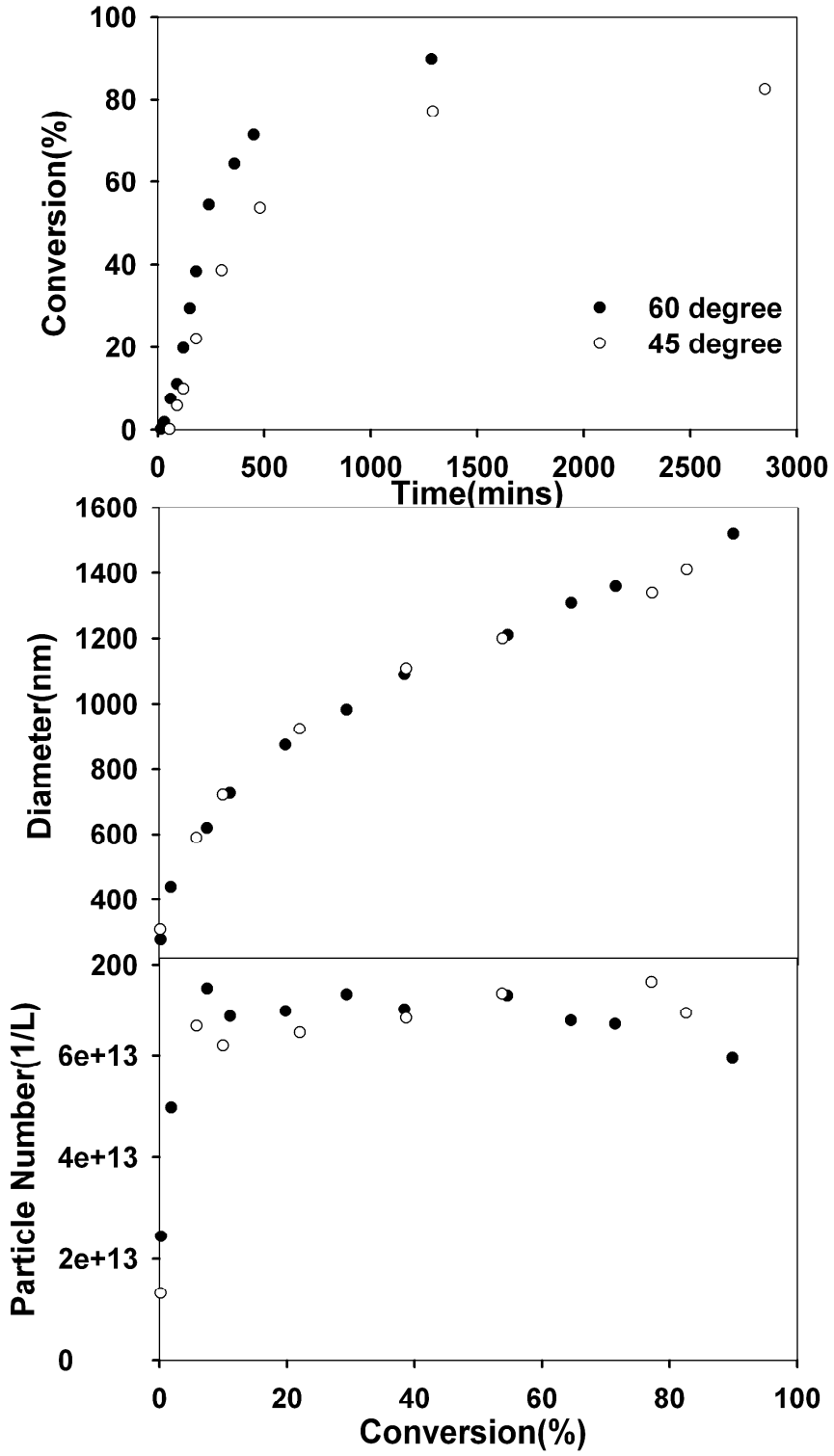
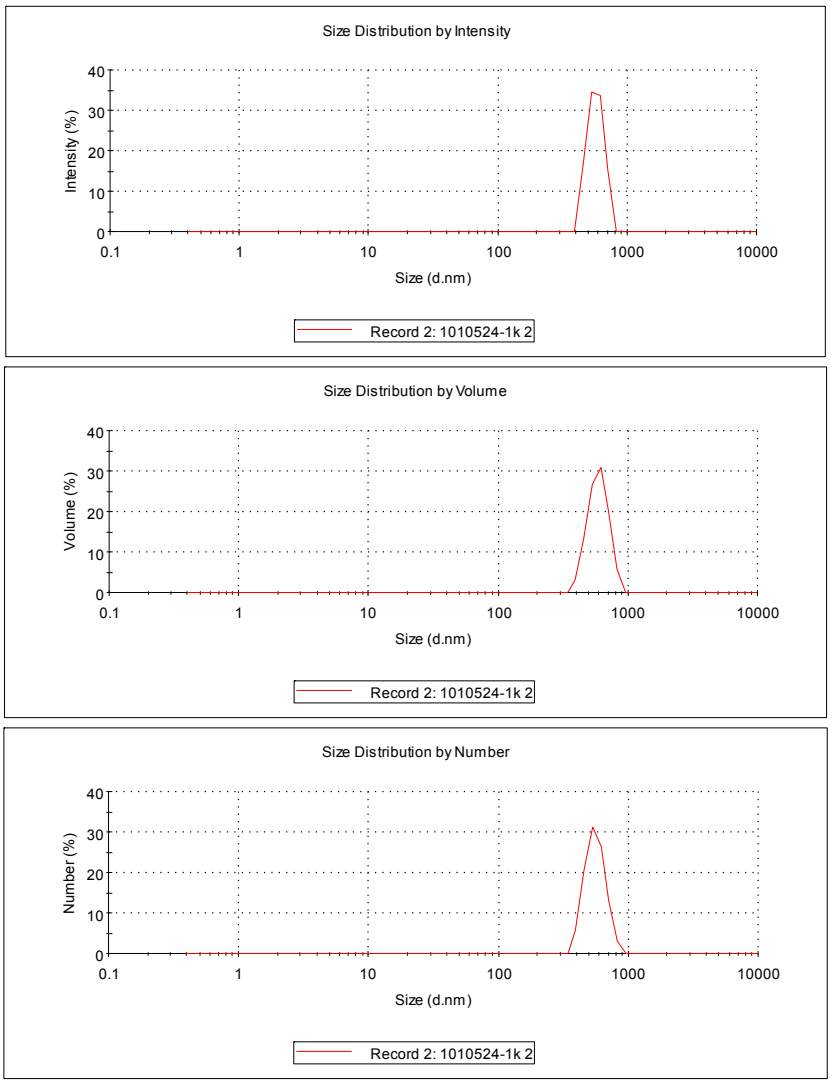


Figure S3. The plots of conversion versus time, diameter, and N_p evolution of AN-PS4 (60 ^oC) and AN-PS8 (45 ^oC).

Table S3. The recipe for soapless dispersion polymerization of styrene in ionic/non-ionic mixed initiation system

Sample code	Methanol (ml)	Styrene (g)	ionic (g)	Non-ionic (g)	Reaction Temperature(^{o}C)	d_n(μm)	CV (%)
VD-PS5	20	5	0.012	0.152	60	/[a]	/
VD-PS6	20	5	0.012	0.076	60	3.27	1.1
VD-PS7	40	5	0.012	0.182	60	2.23-6.85[c]	>50
VD-PS8	40	5	0.018	0.227	60	/[a]	/
VD-PS9 [b]	40	5	0.012	0.152	60	<1, 3.82-4.76[c]	43
VD-PS10	40	6	0.012	0.183	60	3.69-4.53[c]	5.8
VD-PS11	40	5	0.006	0.152	60	/[a]	/
VD-PS12	30	5	0.006	0.152	60	3.60-4.33[c]	6.5
VD-P(S-DVB)1	40	S:4.75 D:0.25	0.012	0.152	60	2.23	<1
	Methanol/ Ethanol(ml)						
AN-PS15	5/45	5	0.025	0.1	60	1.98	<1
AN-PS16	5/45	5	0.025	0.15	60	/[a]	/
VD-PS13	5/45	5	0.012	0.076	60	3.79	1.8
VD-PS14	15/35	5	0.018	0.076	60	4.22-5.98[c]	8.3
	Methanol/ THF(ml)						
VD-PS15	37.5/2.5	5	0.012	0.152	60	/[a]	/
VD-PS16	39/1	5	0.012	0.152	60	1.73-5.32[c]	>50
VD-PS17	39/1	7.5	0.012	0.152	60	3.67	1.4
VD-PS18	39/1	10	0.012	0.152	60	3.12	2.1

[a] Coagulated. [b] 300rpm. [c] Multimodal.



Dn=562.6nm, Dv=589.7nm, Dz=542.5nm, PDI=1.048.

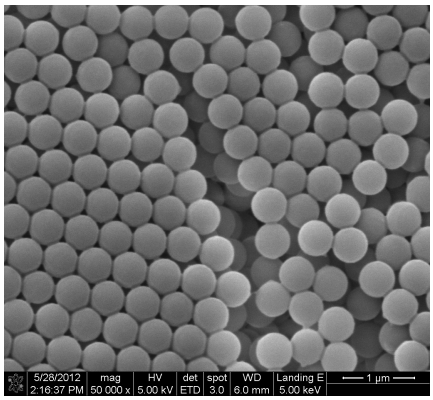
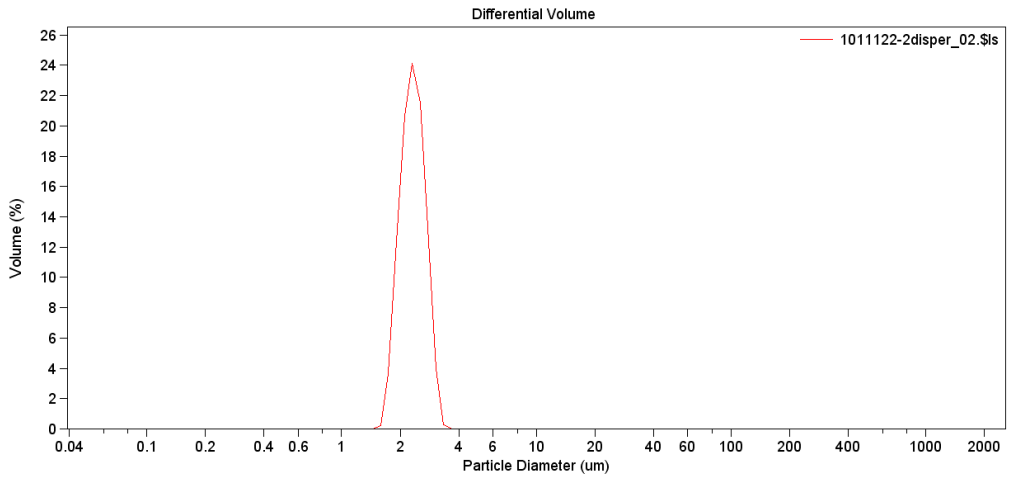
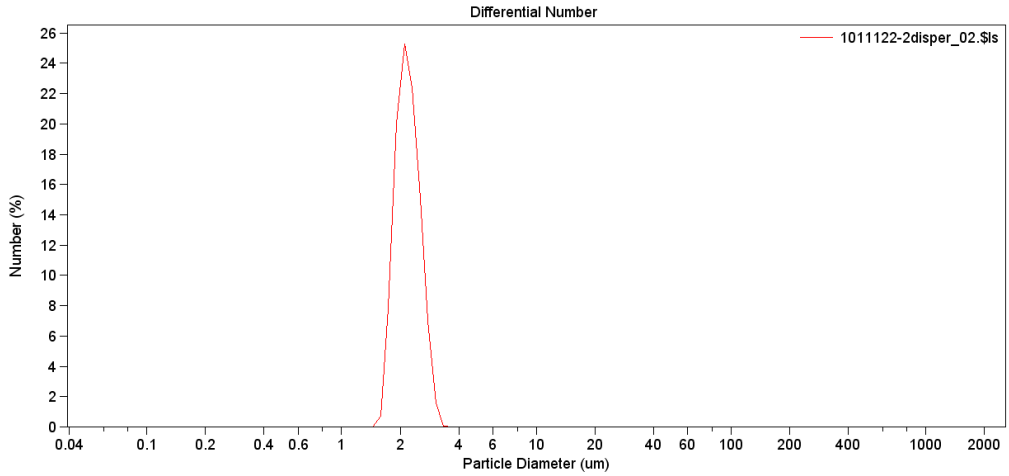


Figure S4. The particle size distribution and SEM image of AN-PS1 obtained from DLS measurement.





Dn=2190nm, Dv=2303nm, PDI=1.05

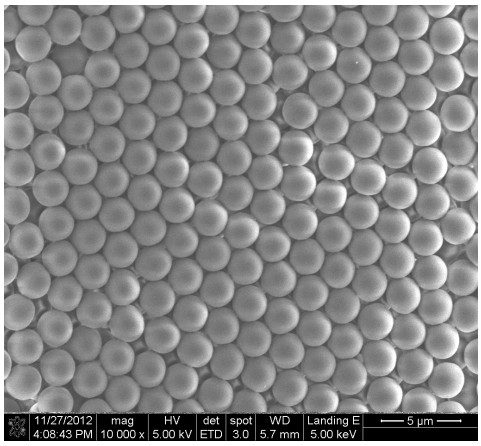


Figure S5. The size distribution of catonic poly(styrene-co-divinylbenzene) latex particles obtained from laser light scattering measurement and its SEM image (VD-P(S-DVB)1).