

Supporting Information

Surfactant-free dispersion polymerization as an Efficient Synthesis Route to a Successful Encapsulation of Nanoparticles

I-Chen Chou¹, Shou-I Chen⁴, Wen-Yen Chiu^{*,1,2,3}

¹Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan

²Institute of Polymer Science and Engineering, National Taiwan University, Taipei,
Taiwan

³Department of Materials Science and Engineering, National Taiwan University,
Taipei, Taiwan

⁴Department of Polymer Solution & Reaction Material & Chemical Research
Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan

Tel: +886-2-23623259

Fax: +886-2-23623259

E-mail: ycchiu@ntu.edu.tw

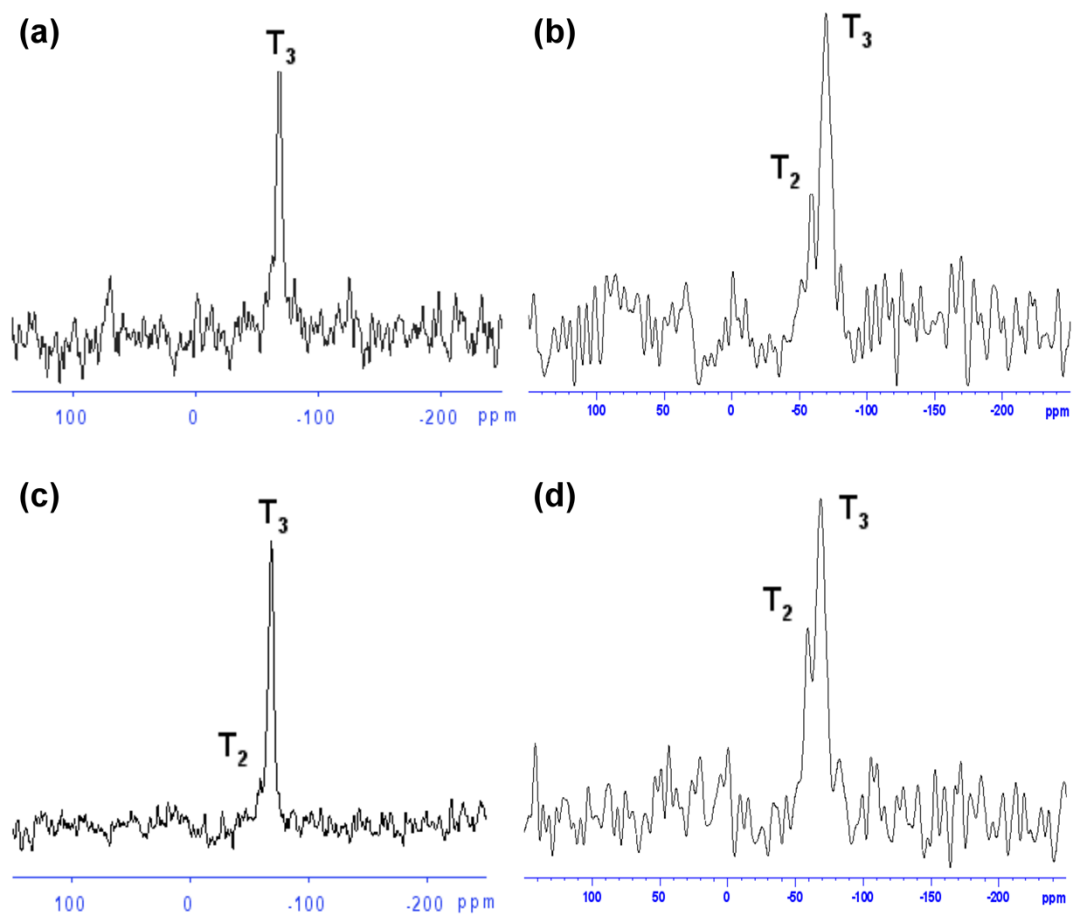


Figure S1. ^{29}Si solid state NMR spectra of 3-(Trimethoxysilyl)propyl methacrylate (MSMA) modified MOGUL[®] L CB. (a) CB 1. (b) CB 2. (c) CB 5. (d) CB 7.

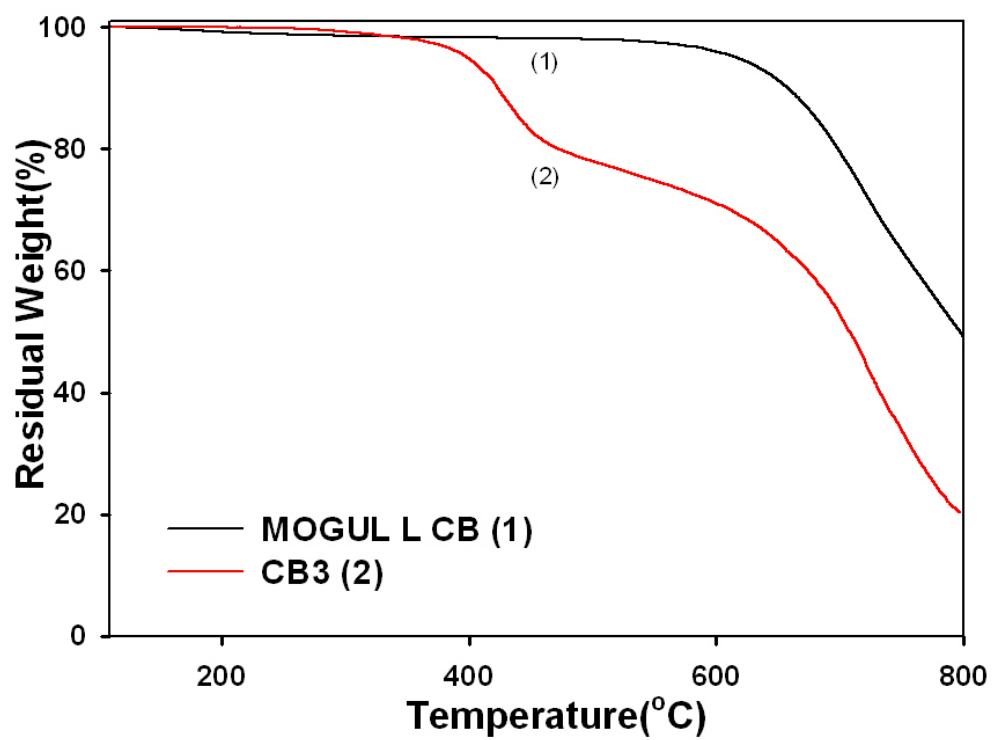


Figure S2. Thermogravimetric Analysis (TGA) analysis of pristine MOGUL[®] L CB and MSMA modified CB3.

Table S1. Recipe for the Silane-Modified SiO₂ Nanoparticles for Encapsulation.^a

Sample Code	Ethanol/Water (ml)	Ammonium Hydroxide (g)	TEOS (g)	Silane (g)	Size (nm) ^b	Zeta Potential (mV) ^c
SiO ₂ -1	30/1.8	0.5	1.44	MSMA/0.5	49.8	-45±6
SiO ₂ -2	30/1.8	0.5	1.44	MSMA/1.5	43.1	-62±8
SiO ₂ -3	30/2.05	0.25	1.44	MSMA/1.5	31.5	-35±6

^a Conditions: Silica formation 3 hours; Silane grafting: overnight; Ambient temperature; Purification through dialysis against methanol (cellulose membrane, MWCO=3500g/mol). ^b Obtained from DLS measurements (Number Average), methanol as dispersant. ^c Obtained from electrophoresis measurements, DI water as dispersant.

Table S2. Recipe for the Silane-Modified TiO₂ Nanoparticles for Encapsulation.^a

Sample Code	Ethanol/Water (ml)	Hydrochloric acid (g)	TTIP (g)	Silane (g)	Size (nm) ^b	Zeta Potential (mV) ^c
TiO ₂ -1	40/1.2	0.15	1	MSMA/1.5	10	40±5
TiO ₂ -2	40/1.2	0.15	1	AEPTS/0.2+MSMA/1.3	8	47±4
TiO ₂ -3	40/1.2	0.15	1	AEPTS/0.5+MSMA/1.0	13	52±6
TiO ₂ -4	40/1.2	0.15	1	MTS/1.0+MSMA/0.5	15	41±5

^a Conditions: Titania formation 3 minutes; Silane grafting: overnight; Ambient temperature; Concentration of hydrochloric acid: 12M; TTIP: Titanium isopropoxide; AEPTS: 3-[2-(aminoethylamino) ethylamino] propyl-trimethoxysilane; MTS: Methoxy(trimethyl)silane; Purification through dialysis against methanol (cellulose membrane, MWCO=3500g/mol). ^b Obtained from DLS measurements (Number Average), methanol as dispersant. ^c Obtained from electrophoresis measurements, DI water as dispersant.

Table S3. Recipe for Soapless Dispersion Polymerization for Encapsulation of nanoparticles (SiO₂/TiO₂) into Polymeric Latexes.^a

Sample Code	Methanol/Water (ml)	Monomer (g)	Initiators (g)	NPs code/ amount (g)	d _n (nm) ^c	PDI ^c	Encapsulation efficiency(%) ^d	Index(%) ^e
PIBSI1 ^b	24/24	2.5	K/0.015	SiO ₂ -1/0.25	735	0.059	41.7	39.2
PIBSI2	24/24	2.5	K/0.015	SiO ₂ -2/0.25	572	0.283	70.5	50.5
PSSI1	43/5	2.5	K/0.015	SiO ₂ -3/0.25	1386	0.173	13.9	11.5
PSSI2	33/15	2.5	K/0.015	SiO ₂ -3/0.25	518	0.124	75.6	66.2
PSSI3	33/15	2.5	K/0.015	SiO ₂ -3/0.36	433	0.192	69.8	56.4
PSSI4	33/15	2.5	K/0.015	SiO ₂ -3/0.14	525	0.067	80.5	75.1
PSTI1	33/15	2.5	A/0.015	TiO ₂ -1/0.25	460	0.135	77.1	66.7
PSTI2	33/15	2.5	A/0.015	TiO ₂ -2/0.25	385	0.168	82.0	68.2
PSTI3	33/15	2.5	A/0.015	TiO ₂ -3/0.25	177	0.131	91.3	79.3
PSTI4	47/1	5	A/0.015	TiO ₂ -2/0.5	495	0.538	84.5	39.0
PSTI5	47/1	5	A/0.015+N/0.3	TiO ₂ -2/0.5	890	0.191	76.9	62.2
PSTI6	40/0	5	V/0.012+D/0.16	TiO ₂ -2/0.5	1250	0.177	85.7	70.5
PSTI7	40/0	5	V/0.012+D/0.16	TiO ₂ -4/0.5	1760	0.134	88.5	76.6

^a Conditions: 100rpm stirring rate; Reaction temperature: 60 °C; K: Potassium persulfate (KPS); A: 2,2'-Azobis(2-methylpropionamide) dihydrochloride (AIBA); V: 2,2'-Azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044); N: 2,2'-Azobisisobutyronitrile (AIBN); D: 2,2'-Azobis(2,4-dimethylvaleronitrile) (ADV). ^b PIBSI: SiO₂-encapsulated Polyisobutyl methacrylate latex ^c Obtained from DLS measurements (Number Average). ^d Determined from the residual weight at 500 °C by thermogravimetric analysis (TGA)

^e Product of Encapsulation efficiency and (1-PDI).