

Electronic Supplementary Information

Preparing Artificial Latexes Using a Switchable Hydrophilicity Solvent

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Content

CO₂ switchability of solvent Cy₂NMe	2
Surface tension plot of SDS in aqueous solution	4
Preparation of artificial latex using conventional emulsion method	5
PBMA as solid polymer	5
Natural rubber as solid polymer	6
Residual solvent in artificial polymer latex	7
Cy ₂ NMe as switchable hydrophilicity solvent	7
2-(Diisopropylamino)ethanol as switchable hydrophilicity solvent	8
Preparation of artificial latex using miniemulsion method	9
Pseudoternary phase diagram	9
Comparison of conventional emulsion method and miniemulsion method	10
References	10

CO₂ switchability of solvent Cy₂NMe

The CO₂-switchable solvent Cy₂NMe is commercially available, reasonably cost-effective and suitable for generating artificial latexes. Compared to primary and secondary amines, tertiary amines such as Cy₂NMe are preferred because they are unable to form carbamates upon reaction with CO₂. Cy₂NMe has an appropriate pK_{aH} value (pK_{aH}=11.03: pK_a of the conjugate acid)¹ to allow it to be reversibly switched between a hydrophobic form that is poorly miscible with water, and a hydrophilic form that is miscible with water at the amine:volume ratios used in our experiments. Cy₂NMe is sufficiently hydrophobic to form a biphasic mixture when mixed with water under air, but with the addition of CO₂ at 1 atm it effectively becomes miscible with water because it is converted to the bicarbonate salt (Figure S1).

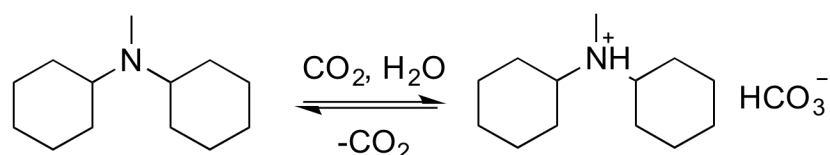


Figure S1. The switching behavior of switchable solvent Cy₂NMe triggered with CO₂.

The conductivity of Cy₂NMe (45 mM) in water was measured at 25 ± 0.5 °C for two cycles of alternating CO₂ and N₂ bubbling. Continuous bubbling of CO₂ ensures that the solution remains saturated with CO₂. The results are shown in Figure S2. The conductivity of the Cy₂NMe solution increased from 2 to 231 μS/cm after CO₂ bubbling for 16 min. It decreased to its initial value upon subsequent bubbling with N₂. Cy₂NMe, an unprotonated amine, is converted to a bicarbonate salt in the presence of CO₂ and water.

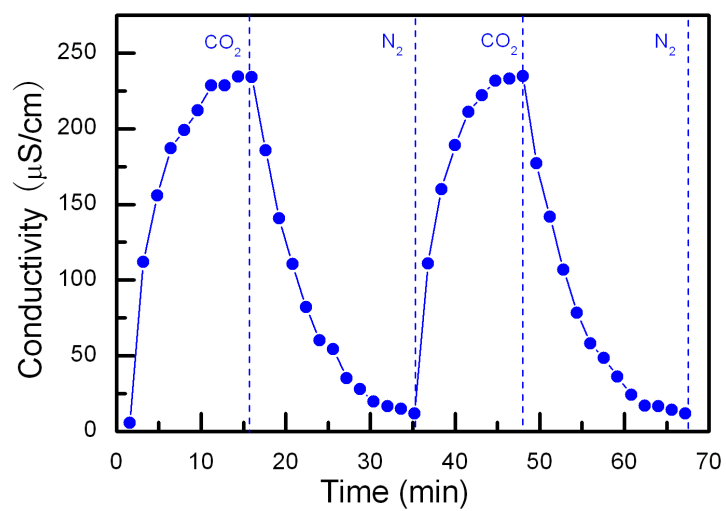


Figure S2. Conductivity of aqueous solutions of Cy₂NMe (45 mM) at 25 ± 0.5 °C as a function of time during two cycles of sparging with CO₂ (flow rate 90 mL/min) followed by N₂ (flow rate 90 mL/min).

Surface tension plot of SDS in aqueous solution

Air/water surface tensions were measured with the Wilhelmy plate technique using an automatic surface tensiometer (TensioCAD). Measurements were taken at 25 ± 0.5 °C until a constant surface tension value was reached. The critical micelle concentration (CMC) values were taken at the intersection of the linear portions of the surface tension plots against the logarithm of the surfactant concentration. Stock solutions were diluted continuously with pure water and the air/water surface tension at each concentration was obtained by averaging three measurements. As Figure S3 shows, the CMC of SDS is 0.78 mmol/L, and the lowest surface tension (at concentrations beyond the CMC) is 37.2 mN/m.

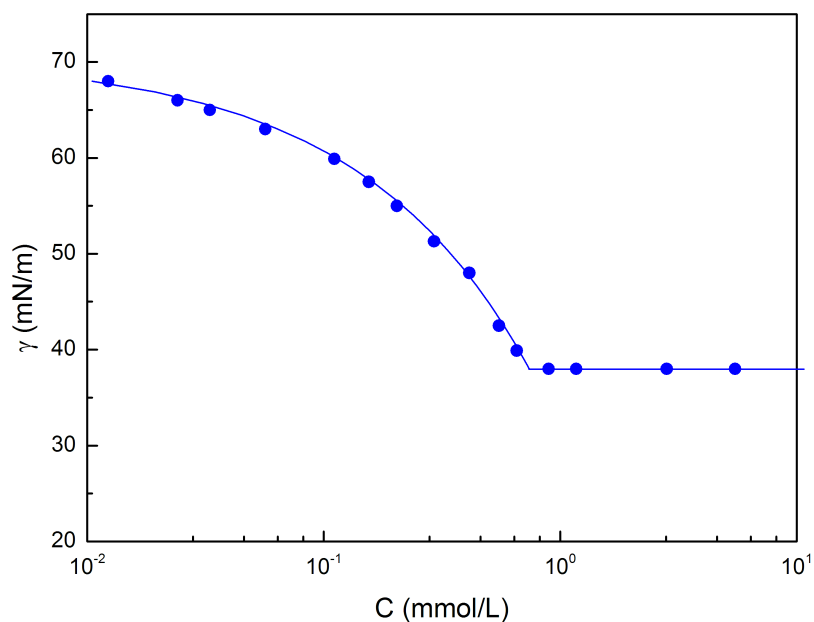


Figure S3. Surface tension of aqueous solution of SDS under air at 25 ± 0.5 °C.

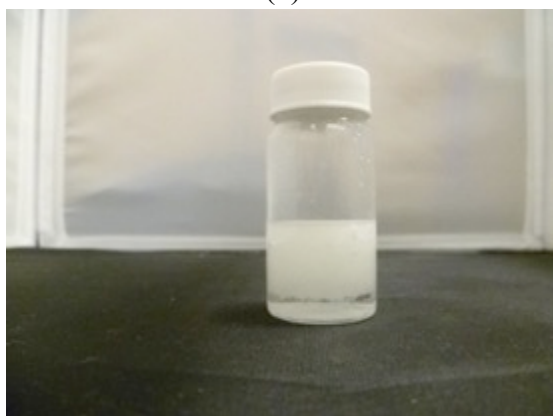
Preparation of artificial latex using conventional emulsion method

PBMA as solid polymer

Figure S4 shows images of the artificial PBMA latex prepared using the emulsion method.



(a)



(b)



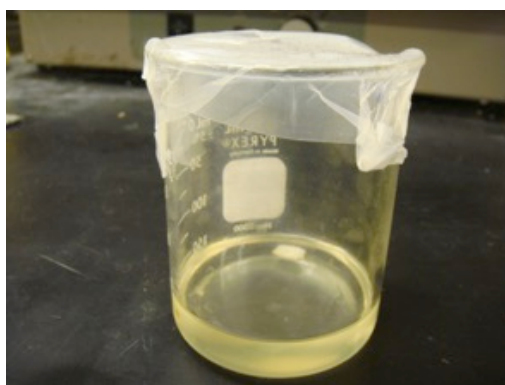
(c)

Figure S4. Images of PBMA latexes using Cy₂NMe in different stages: (a) emulsion containing PBMA (6.0 g), Cy₂NMe (30.0 g), the surfactant SDS (1.5 g) and water (100.0 g); (b) after addition of CO₂ (flow rate, 90mL/min), the polymer has separated from the water phase; (c) the partially phase separated polymer was added to 30.0 g pure water and redispersed.

Natural rubber as solid polymer



(a)



(b)



(c)

Figure S5. Images of different stages in the preparation of artificial latex of natural rubber using Cy_2NMe . (a) Natural rubber (6.0 g) added to 30.0 g Cy_2NMe . (b) The rubber dissolved after 30 min. (c) The solution of rubber mixed with water (100.0 g), and the surfactant SDS (1.5 g). Following sonication (10 min) and addition of CO_2 (flow rate, 90mL/min), the phase separated polymer was added to 30.0 g pure water and redispersed.

Figure S5 shows the artificial latex of natural rubber prepared using the emulsion method.

Residual solvent in artificial polymer latex

Cy₂NMe as switchable hydrophilicity solvent

The amount of residual Cy₂NMe was determined by ¹H NMR spectroscopy. The artificial PBMA latex (10.0 g) prepared via conventional emulsion was dried at 150 °C for 4 h until the weight did not decrease further. A ¹H NMR spectrum of the dried latex was acquired in CDCl₃ with DMSO as an internal standard (Figure S6).

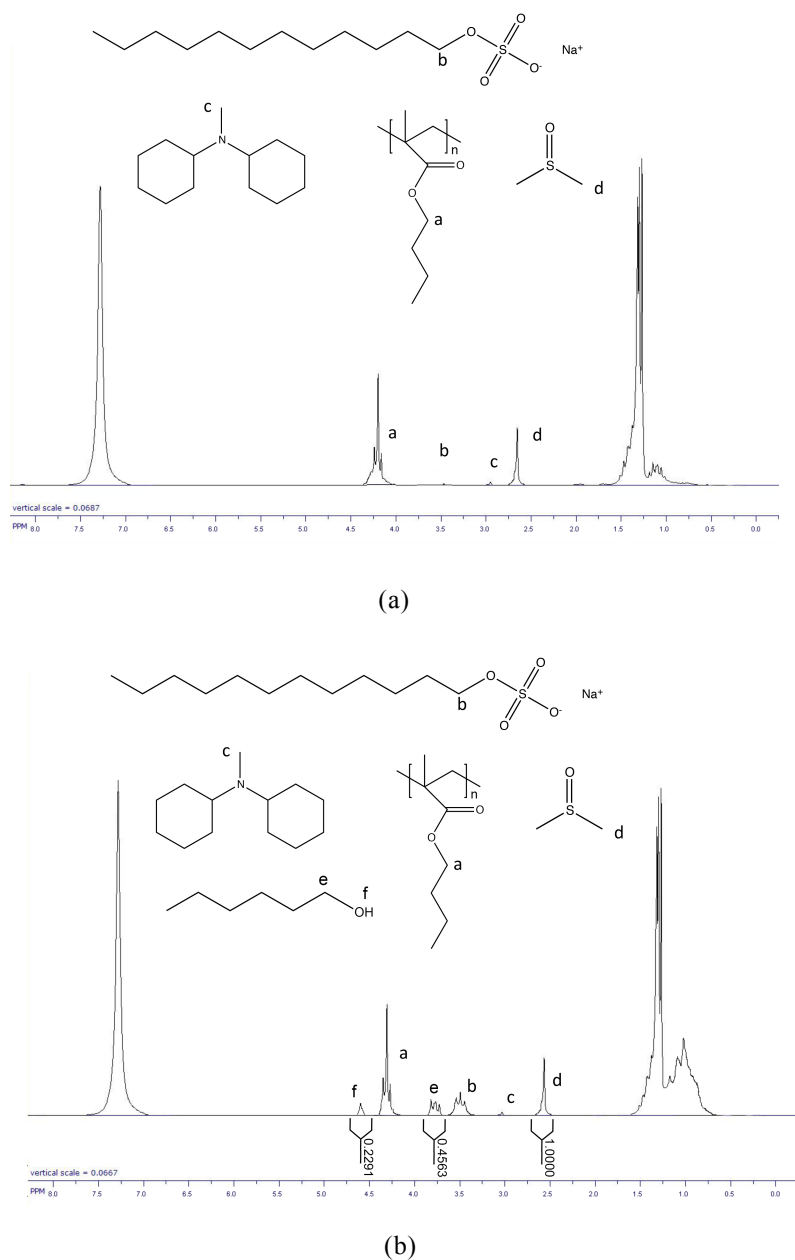


Figure S6. ¹H NMR spectrum of artificial PBMA latex using Cy₂NMe in CDCl₃. (a) Artificial latex prepared via conventional emulsion (the first entry in Table 3). (b) Artificial latex prepared

via miniemulsion. DMSO was the internal standard used to calculate the residual Cy₂NMe.

2-(Diisopropylamino)ethanol as switchable hydrophilicity solvent

Table S1. The particle size of PBMA latexes prepared with 2-(diisopropylamino)ethanol using a conventional emulsion.^[a]

Stage	Particle size (dz)	PDI	Residual SHS (wt%) calculated by elemental analysis ^[b]
Original	853 nm	0.48	0.7
After cycle 1	913 nm	0.37	0.2
After cycle 2	956 nm	0.65	<0.1 ^[c]

[a] The emulsion contained PBMA (3.0 g), 2-(diisopropylamino)ethanol (10.0 g), surfactant SDS (1.5 g) and water (15.0 g). After addition of CO₂ (flow rate 90 mL/min), the polymer separated from the water phase; the separated polymer was added to 6.0 g pure water and redispersed. This latex was then washed again in multiple cycles; in each cycle the mixture was sparged with CO₂ for 15 min, and then centrifuged for 3 min; the aqueous layer was removed and the polymer particles were redispersed into 6.0 g pure water with 0.4 g SDS.

[b] The elemental analysis was conducted using a Perkin Elmer CHNS/O (2400 series) using helium as carrier gas.

[c] The detection limit of elemental analysis for N is 0.01 wt.%, and thus the detection limit of element analysis for 2-(diisopropylamino)ethanol is 0.1 w.t.%.

Preparation of artificial latex using miniemulsion method

Pseudoternary phase diagram

We studied the phase behaviour for the system containing five components and prepared the pseudoternary phase diagram (Figure S7) following the method described by Pons et al..² The surfactant/cosurfactant and solvent/polymer ratios were kept constant. The experiment was conducted at 25 °C with stirring (at a speed of ~700 rpm). After each addition of water, the samples were stirred and allowed to equilibrate for at least 12 h. Isotropic phases were assigned by visual inspection.

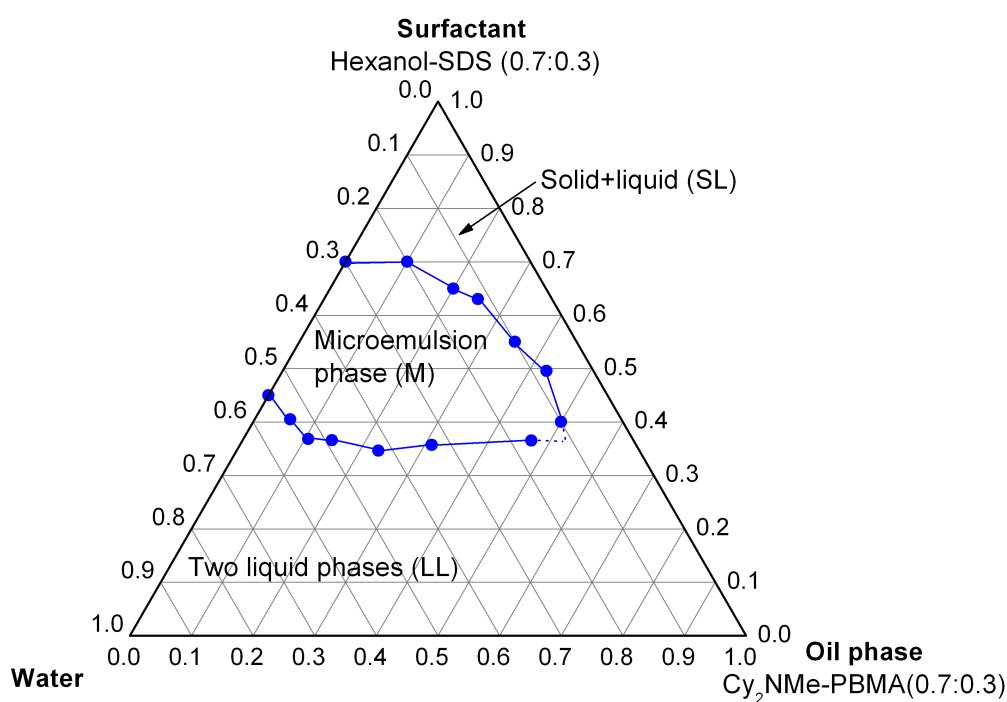


Figure S7. Pseudoternary phase diagram (weight ratio) for water/hexanol-SDS (weight ratio=7:3)/Cy₂NMe-PBMA (weight ratio=7:3) obtained at 25 °C.

Comparison of conventional emulsion method and miniemulsion method

Table S2. Zeta-potential and particle size of PBMA latexes prepared by CO₂-switchable solvent using either a conventional emulsion or a miniemulsion.

	Zeta-potential	Particle size range by SEM	Mean Particle Diameter by DLS (d _z)	PDI
Conventional emulsion	-42 mV	100-1000 nm	975 nm	0.450
Miniemulsion	-54 mV	200-300 nm	242 nm	0.072

References

1. Calculated via <https://ilab.acdlabs.com/iLab2/index.php> (accessed December 2016).
2. R. Pons, I. Carrera, J. Caelles, J. Rouch and P. Panizza. *Adv. Colloid Interface Sci.*, 2003, **106**, 129.