

Supporting Information

Part 1. Description on materials used in the present work

Table S1 Details of the materials used in the experiments

Chemicals	Abbreviation in the text	Grade of materials	Manufacturer
Trihydroxymethyl propane triacrylate	TMPTA	Not specified	Tianjiao chemicals, Tianjin, China
Styrene	St	Chemical pure	Beijing chemicals, Beijing, China
Anhydrous ethanol	EtOH	Chemical pure	Qiuzhu Corp. of science & technology, Tianjin, China
Azobisisobutyronitrile	AIBN	Chemical pure	Damao chemicals, Tianjin, China
Ethyl benzene	EB	Chemical pure	Fuyu chemical Corp., Tianjin, China
Cyclohexane, xylene and toluene		Chemical pure	All from Fuyu Chemical Corp., Tianjin, China
Water	H ₂ O	Double distilled	Done in the laboratory

Part 2. Description on precipitation polymerization and sample characterization

Polymerizations were carried out in glass bottles of 120 mL capacity. In each was charged 2 mL of monomers TMPTA and St at varied mass ratios, along with 2.0 wt% azobisisobutyronitrile (AIBN) relative to the monomers. 98 mL of ternary solvent mixture consisting of distilled H₂O, anhydrous EtOH and ethyl benzene (EB) at different volume ratios was then added into each bottle. After complete dissolution of the monomers and the initiator followed by nitrogen purge for 5 min, all bottles were sealed off and located into a thermostat, whose temperature was increased to 70 °C within 1 h. The initially homogeneous reaction mixtures turned milky white within 5 to 10 min after reaching 70 °C, depending on the formulation. Unless otherwise stated, all reactions were run for 4 h. In some parallel runs, EB was replaced by a same volume of an alternative solvent, including cyclohexane, xylene, toluene, ethyl benzene, acetone, acetonitrile, ethyl acetate, butanone, octanol and trichlormethane, 10 solvent in total.

Sample characterization: Upon polymerization, sample was taken out from the reaction bottle and a few drops of the sample placed on a glass plate. After evaporation of the solvents at room temperature, the sample was coated by gold sputtering for 400 seconds under 10 KV voltage prior to examination via scanning electron microscopy (SEM, Hitachi S-2500, Japan). The microsphere size (D_n) and size distribution (D_w/D_n) was determined by counting at least 200 microspheres from the SEM micrographs. To separate the

microspheres out from the polymerization medium, the final product was subjected to centrifugation for 5 minutes at 12,000 r/min (Avanti J301, Beckman). The supernatant was dried up at 100 °C for 24 h in order to evaluate the yield of the soluble polymer, and the sedimentated microspheres were also dried up to get their yield. The sum of the two yields was considered as the monomer conversion. To get the soluble polymer in EB and water-ethanol, the supernatant was further subjected to centrifugation for 15 minutes at the same speed, followed by shelf-standing for 3 h. The top EB phase and the bottom phase were separated. The soluble polymer in each phase was determined by gravimetry. To observe the interior structure of the assembled microspheres, the dry microspheres were put into a liquid nitrogen container and kept there for 3 min, and hit using a hammer. The fractured microspheres were examined under the same SEM.

Part 3. SEM microspheres obtained using different organic solvent incorporated in H₂O-EtOH binary solvent mixture. Precipitation polymerization was carried out in a binary mixture of H₂O (25.8 mL) and EtOH (60.2 mL) at H₂O/EtOH of 3/7 by volume. 2 wt% of St and TMPTA were used as the monomers at TMPTA/St of 30/70 by mass, and 12 mL of the third solvent was added to the binary solvent of H₂O/EtOH. The third solvents used included cyclohexane, ethyl acetate, acetone, butanone, trichloromethane, octanol, acetonitrile, ethyl benzene, xylene and toluene. Experimental results revealed that self-assembly of the primary particles was observed only when ethyl benzene, xylene or toluene was used as the third solvent. For a visual illustration, selected SEM pictures of the outcome microspheres are given in Fig. S1.

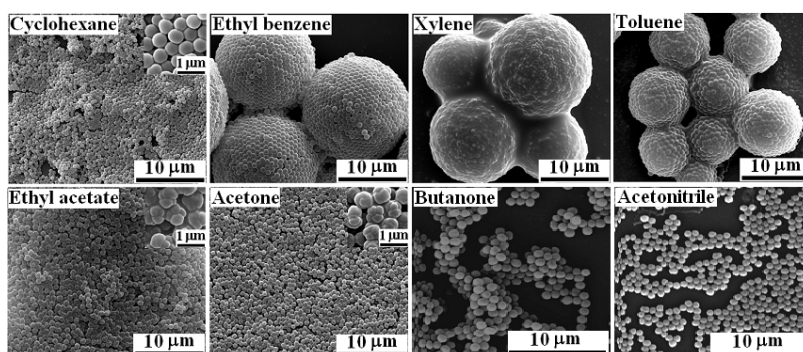


Fig. S1 SEM pictures of resulting microspheres when doing precipitation polymerization of TMPTA-St in H₂O-EtOH in the presence of a third solvent (shown on the pictures)

Part 4. Solubility test of a third solvent in H₂O-EtOH binary solvent. In 100 mL of H₂O-EtOH binary solvent in a centrifuge tube, 25 mL of a third solvent were added. The ternary solvent was sonicated at 40 KHz for 5 min (KQ-100, Kunshan Instruments, China), and left for shelf-standing for 1 h, 4 h and 24 h,

respectively, followed by centrifugation of the sample at 12,000 r/min for 15 min. The sample eventually phase separated into two phases at end of this process, H₂O-EtOH at the bottom and an organic phase on the top. The top phase was carefully transferred into a pear-shaped separatory funnel and then left for shelf-standing for 24 h in order to separate out the thimbleful amount of H₂O-EtOH entrained with the transfer of the upper phase. The whole amount of the organic phase thus obtained was considered as the amount of the third solvent exceeding its solubility in H₂O-EtOH, and denoted as solvent separated from H₂O/EtOH. The same test was done using different H₂O/EtOH volume ratios of 2/8, 3/7 and 4/6. Results are given in Table S2. From these results, it was easily seen that the droplets were possibly present only for cyclohexane when mixed with the binary solvent at H₂O/EtOH volume ratios of 2/8; and with increase in water content in H₂O-EtOH, the solubility of certain tested solvents was significantly reduced, and thus the solubility of xylene, toluene and EB was all lowered to be less than 25 mL in 100 mL of the mixed H₂O-EtOH solvent when its H₂O/EtOH volume ratio increased to 3/7 or higher (with more water), i.e. excessive amount of xylene, toluene or EB was available for droplet formation. However, for the rest of the six solvents, they were thorough miscible with H₂O-EtOH regardless of H₂O/EtOH ratios tested as shown in Table S2.

Table S2 Amount of a third solvent separated out with 25 mL of the solvent mixed with 100 mL of H₂O-EtOH binary solvent

Solvents	Solvent separated (mL) in H ₂ O/EtOH of different volume ratio					
	H ₂ O/EtOH=2/8		H ₂ O/EtOH=3/7		H ₂ O/EtOH=4/6	
	4 h ^a	24 h	4 h	24 h	4 h	24 h
Cyclohexane	16.0	15.0	21.0	20.0	23.0	23.0
Ethyl benzene	0	0	16.5	16.5	22.5	22.5
Xylene	0	0	16.0	16.0	21.5	21.0
Toluene	0	0	13.5	13.0	21.0	20.5
Acetone, acetonitrile, ethyl acetate, butanone, octanol, trichlormethane	0	0	0	0	0	0

^a time of shelf-standing before the sample was centrifuged.

Since the experiments were mostly done with H₂O/EtOH volume ratio at 3/7, the results in Table S2 obtained at H₂O/EtOH volume ratio at 3/7 were further treated to give the amounts of a third solvent dissolved in and separated out with 25 mL of the solvent mixed with 100 mL of H₂O-EtOH binary solvent at 3/7 volume ratio (Table S2). And the amount dissolved in 100 mL of H₂O-EtOH was further transformed to

the equivalent in 86 mL of H₂O-EtOH (Data in the right column in Table S3), the real amount used in the experiments of the present work.

Table S3 Amounts of a third solvent dissolved in and separated out with 25 mL of the third solvent mixed with 100 mL of H₂O-EtOH binary solvent at 3/7 volume ratio (obtained from Table S2)

Solvents	Solvent (mL) separated from		Solvent (mL) dissolved in		Solubility in 86 mL of H ₂ O-EtOH	
	4 h ^a	24 h	4 h	24 h	4 h	24 h
Cyclohexane	21.0	20.0	4.0	5.0	3.4	4.3
Ethyl benzene	16.5	16.5	8.5	8.5	7.3	7.3
Xylene	16.0	16.0	9.0	9.0	7.7	7.7
Toluene	13.5	13.0	11.5	12.0	9.9	10.3
Acetone, acetonitrile, ethyl acetate, butanone, octanol, trichlormethane	0	0	>25		>21.5	

^a time of shelf-standing before the sample was centrifuged.

Table S4 EB availability for droplet formation in precipitation polymerization of St-TMPTA in H₂O-EtOH binary solvent with varied EB amount incorporated obtained from Table S3

Run	H ₂ O (mL)	EtOH (mL)	EB (mL)	EB solubility	EB (mL) available for droplet formation
A1	27.6	64.4	6.0	7.8	0.0
A2	27.0	63.0	8.0	7.7	0.3
A3	26.4	61.6	10.0	7.5	2.5
A4	25.8	60.2	12.0	7.3	4.7
A5	25.2	58.8	14.0	7.1	6.9
A6	24.6	57.4	16.0	7.0	9.0
A7	24.0	56.0	18.0	6.8	11.2
A8	22.8	53.2	22.0	6.5	15.5
A9	21.0	49.0	28.0	6.0	22.0

Part 5. Evolution of colloidosomes formation during the process of polymerization.

To study the evolution of the primary particles and formation of the assembled colloidosomes, precipitation polymerization was carried out in a binary mixture of H₂O (25.8 mL) and EtOH (60.2 mL) at H₂O/EtOH of 3/7 by volume. 2 wt% of St and TMPTA were used as the monomers at TMPTA/St of 30/70 by mass, and 12 mL of the third solvent was added to the binary solvent of H₂O/EtOH. Samples were taken at different polymerization time and subjected to SEM observation (Figure S2).

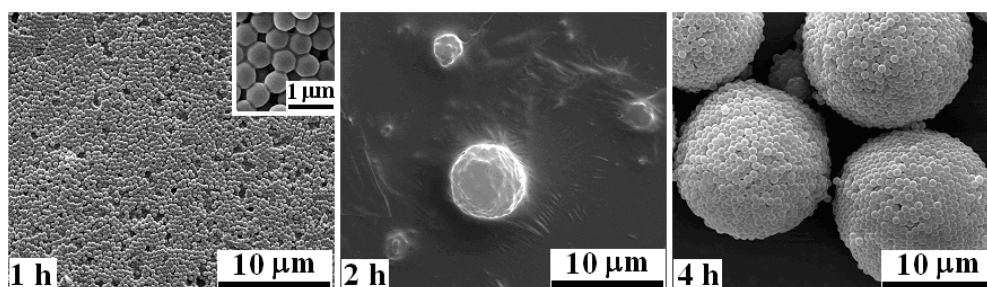


Figure S2. SEM pictures of the microspheres taken at different polymerization time (shown on the pictures)

Part 6. Solubility parameters of the components in the polymerization system

Table S5 Solubility parameters of monomers and solvents and observation of self-assembly of the in-situ formed primary particles

Solvent	Solubility parameter (MPa ^{1/2})	Self-assembly observed	References
Cyclohexane	16.8	No	1 (given below this Table)
Xylene	18.0	Yes	
Toluene	18.2	Yes	
Ethyl benzene	17.8	Yes	
Ethyl acetate	18.2	No	1
Butanone	19.0	No	
Acetonitrile	24.6	No	1
Water	47.9		1
Ethanol	26.6		1
H ₂ O/Ethanol (3/7)	33.0		2
Styrene	19.0		1
TMPTA	22.1		3
TMPTA/St (3/7)	19.8		2

1. J. Brandrup, E. H. Immergut and E. A. Grulke. *Polymer Handbook* (Forth Edition), New York: John Wiley & Sons, Inc. 1999, pp. VII/698-701.

2. Calculated using the equation for the solubility parameter of the mixed solvents:

$$\delta_{\text{mix}} = \delta_1\phi_1 + \delta_2\phi_2 + \delta_3\phi_3 \dots$$

Where, δ_{mix} is the solubility parameter of the solvent mixture, δ_1 that of the solvent 1, ϕ_1 the volume fraction of the solvent 1 in the mixture.

3. S. S. Shim, Y. H. Cho, J. H. Yoon and B. K. Kim, *Eur. Polym. J.*, 2009, **45**, 2184.