

Electronic Supplementary Information

Water-Borne Thiol-isocyanate Click Chemistry in Microfluidics: Rapid and Energy-efficient

Preparation of Uniform Particles

Jiaojun Tan^a, Chunmei Li^a, Hui Li^a, Hao Zhang^a, Junwei Gu^a, Baoliang Zhang^a, Hepeng Zhang^a, Qiuyu Zhang^{a*}

^a Key Laboratory of Applied Physics and Chemistry in Space of Ministry of Education, School of Science, Northwestern Polytechnical University,

710072 Xi'an, Shaanxi, China.

[*qyzhang1803@gmail.com](mailto:qyzhang1803@gmail.com).

Preparation of uniform particles

For an example of TMMP-IPDI system, particles were manufactured via a simple microfluidic composed of tube with inner diameter of 600 μm and 32 gauge needle. First, 10 ml H_2O and 2mL TEA was pre-placed in the receiving beaker, and 100 ml syringe of continuous phase was started at a pre-set flow rate. Subsequently, 10 ml syringe of disperse phase was started, and the generated monomer droplets were collected in the receiving beaker when they became uniform. After collection, particles were placed in the beaker for another 10 min to get a thorough solidification. Finally, the obtained particles were purified by repeating three cycles of washing-redispersion using water and ethanol, respectively.

Results

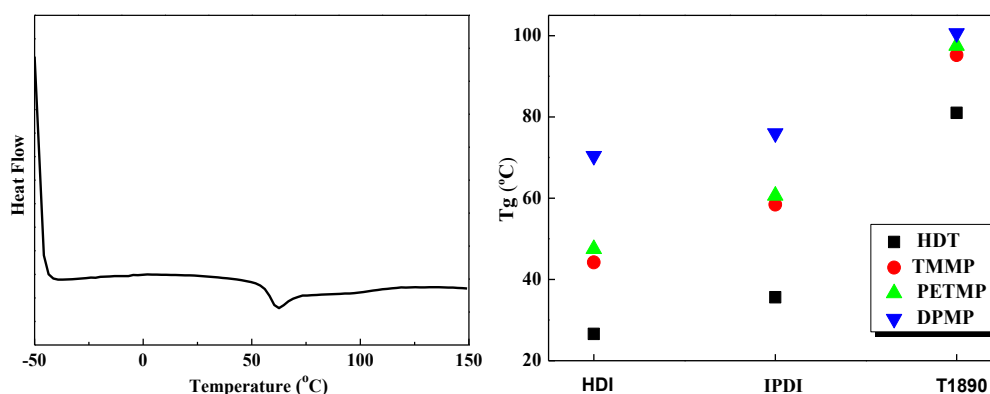


Figure SI-1. (A) The DSC curve of particles obtained by TMMP-IPDI click chemistry. (B) Tg of particles prepared with different thiol and isocyanate monomers. Condition used: Stoichiometric thiol and isocyanate monomers and toluene (20 wt.%) were used as disperse phase. 5 wt.% SDS aqueous solution was used as continuous phase. The tube adopted had an inner diameter of 600 μm , and the needle was 32 gauge.

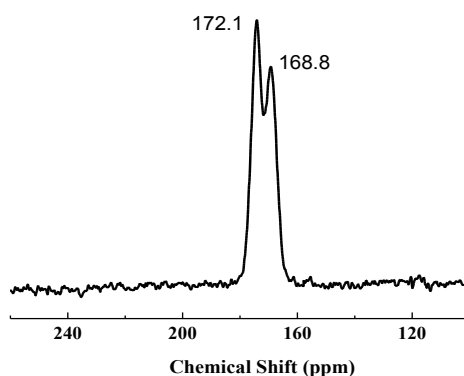


Figure SI-2. The MAS Solid-state ^{13}C NMR spectrum of TMMP-HDI particles. Condition used: Stoichiometric thiol and isocyanate monomers and toluene (20 wt.%) were used as disperse phase, and the method was the same as particles in Figure SI-1.

Table SI-1. The dispersity information of particles prepared with different flow rates of continuous phase

| Flow rate (mL min^{-1}) | 0.5 | 1.0 | 1.5 | 2.0 |
|------------------------------------|-------|------|------|-------|
| Dispersity information(CV) | 17.3% | 8.4% | 4.6% | 15.6% |

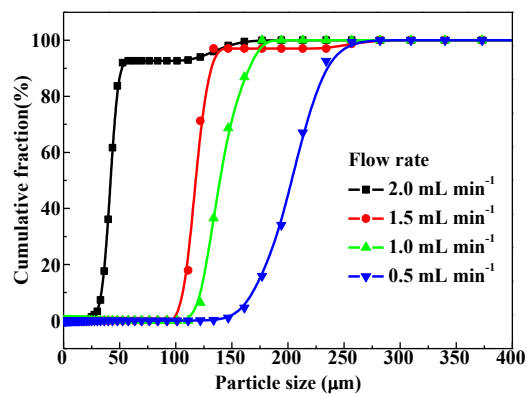


Figure SI-3 Cumulative curve of particles prepared with different flow rates of continuous phase

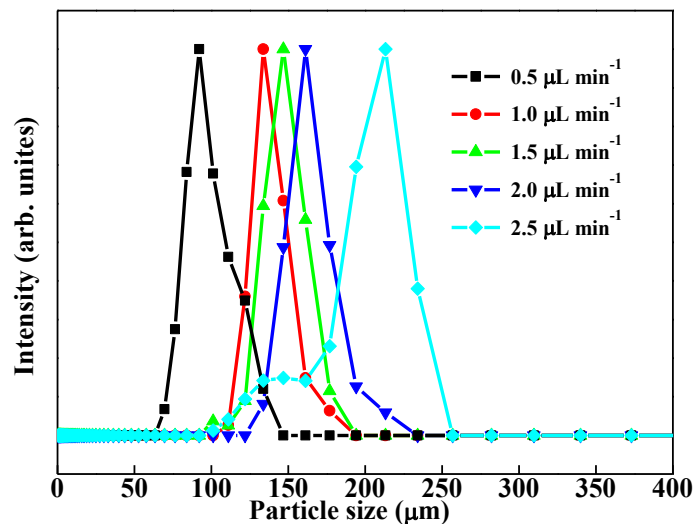


Figure SI-4 Particle size distributions for TMMP-IPDI system with different flow rates of disperse phase: ■(0.5 $\mu\text{L min}^{-1}$), ●(1.0 $\mu\text{L min}^{-1}$), ▲(1.5 $\mu\text{L min}^{-1}$), ▼(2.0 $\mu\text{L min}^{-1}$), ◆(2.5 $\mu\text{L min}^{-1}$). Condition used: TMMP (43.4 wt.%), IPDI (36.6 wt.%) and toluene (20 wt.%) were taken as the disperse phase. The flow rate of continuous phase was 1.5 mL min^{-1} . 5 wt. % SDS aqueous solution was used as continuous phase. The tube adopted had an inner diameter of 800 μm , and the needle was 30 gauge.

Table SI-2. The dispersity information of particles prepared with different flow rates of continuous phase

| Flow rate (mL min^{-1}) | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 |
|------------------------------------|-------|-------|------|-------|-------|
| Dispersity information (CV) | 14.0% | 15.3% | 9.6% | 15.8% | 24.8% |

Table SI-3. The dispersity information of particles with thiol monomers of different functionalities

| Formula | HDT | TMMP | PETMP | DPHP |
|---------------------------------|-------|------|-------|-------|
| Dispersity information (CV) | 14.0% | 4.6% | 9.4% | 16.8% |
| Mean diameter (μm) | 144 | 131 | 270 | 352 |

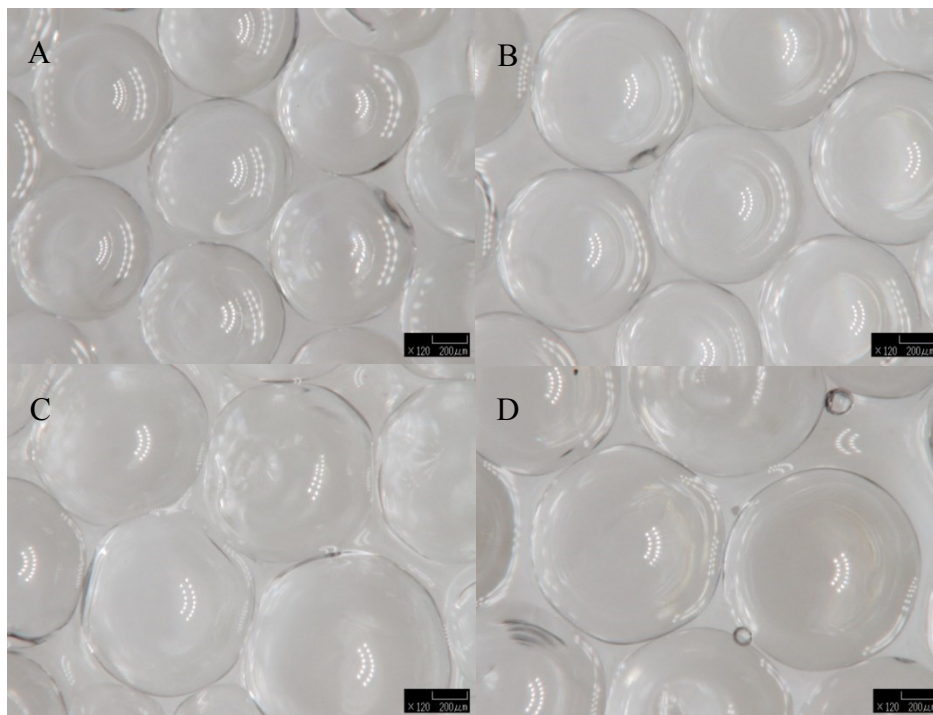


Figure SI-5. The optical microscope images of uniform particles with different flow rates of continuous phase: (A) 2.0, (B) 1.5, (C) 1.0 and (D) 0.5 mL min⁻¹. Condition used: TMMP (43.4 wt.%) ,IPDI (36.6 wt.%) and toluene (20 wt. %) were used as the disperse phase, and the flow rate of disperse phase was 5μL min⁻¹. The tube adopted had a diameter of 1500 μm, and the needle was 30 gauge.

Table SI-4 Molecular weights and molecular weight distributions of non-crosslinked particles

| Sample | M _n | M _w | PDI |
|----------|----------------|----------------|------|
| HDI-HDT | 1779 | 3665 | 2.06 |
| IPDI-HDT | 2004 | 4127 | 2.15 |

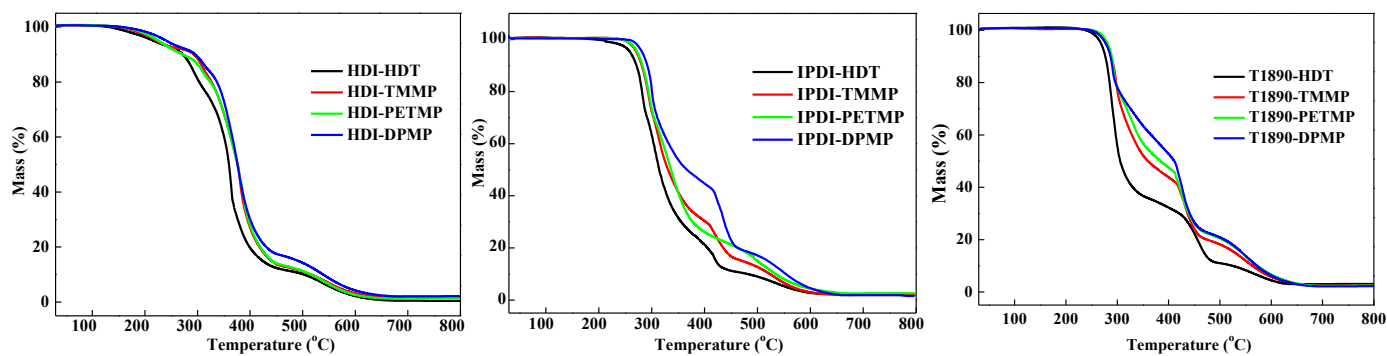


Figure SI-6 TGA curve of particles prepared with different thiol and isocyanate monomers