Supplementary Materials for

# Rapid preparation of waterborne polyurethane dispersions using continuous flow microreaction technology

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# Experimental

## Materials and devices

Polypropylene glycol (PPG, $M_n$=2000 g $mol^{-1}$, 99.0%) was purchased from Shandong Bluestar Dongda Chemical Co. Ltd (China). 2,2-Bis(hydroxymethyl)propionic acid (DMPA, 98.0%) was purchased from BIDE (China). Hydrazine hydrate ($N_2H_4 \cdot H_2O$, 80.0%) was purchased from Tianjin Damao chemicals reagent factory (China). Hydrochloric acid standard solution (0.1 mol $L^{-1}$) was purchased from Bolinda (China). Tetrahydrofuran (THF, 99.9%) was purchased from OCEANPAK (Sweden). Toluene (AR) was purchased from Anjiehui (China). Isophorone diisocyanate (IPDI, 99.0%), N,N-Dimethylformamide (DMF, 99.9%), Butane-1,4-diol (BDO, 99.7%), Triethylamine (TEA, 99.5%), Dibutylamine (99.0%), Isopropanol (IPA, 99.5%), Stannous octoate (T-9, 95.0%), Dibutyltin dilaurate (T-12, 95.0%), Triethylenediamine (DABCO, 98.0%), 1,8-diazabicyclo(5,4,0)undec-7-ene (DBU, 99.0%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 97.0%) and Triphenylbismuthine (TPB, 98.0%) was purchased from Macklin (China). PPG and BDO were dried and degassed at 120 °C under vacuum for 2 h. Other reagents were used without further purification.

Plunger pumps were purchased from Jingjin Technology Co., Ltd. Stainless steel tubing (i.d. 1 mm and o.d. 3 mm, Jiangsu Yongshang Steel Tube Enterprise Store). Micromixers and microreactors were fabricated by Hangzhou Lushan Technology Co., Ltd. Peristaltic pump were purchased from Kamoer. Continuous flow reactor includes microreactor with microstructure inside and microtube reactor made of 5 m stainless steel coil. Microtube reactor is also a type of microreactor in the broad sense.

## Characterization

The content of NCO groups (%) in the prepolymer was determined using the dibutylamine back titration. The particle size and distribution of emulsions were characterized by a nano particle size analyzer of Brookhaven BI-200SM. Attenuated Total Reflection-Fourier-transform infrared (ATR-FTIR) spectroscopies of PU films were obtained in an iS50R spectrometer of Themor-Filsher in transmission mode. The thermal decomposition behavior of the WPU films was measured by a thermogravimetric analyzer (TGA) of Perkin Elmer in the temperature range of 30-60 °C, heating rate 10 °C $min^{-1}$ and nitrogen atmosphere. The glass transition temperature ($T_g$) of the film was measured by differential scanning calorimetry (DSC) of Perkin Elmer. At the beginning of the test, first eliminated the material's thermal history, then cooled it down to -70 °C at a rate of 10 °C $min^{-1}$, and then heated it up to 30 °C at a rate of 10 °C $min^{-1}$. All the above processes were carried out under $N_2$ atmosphere. Gel permeation chromatograph (GPC) estimated the average molecular weight ($M_n$) and average molecular weight ($M_w$) of WPU film by using Agilent PLgel MIXED-B series chromatographic columns and polystyrene standard calibration curves. The polymer dispersibility index (PDI) was calculated as the ratio of $M_w$ to $M_n$. The calibration standard for GPC analysis was polystyrene in tetrahydrofuran (THF) eluent at the flow rate of 1.0 ml $min^{-1}$ at 40 °C. The crystallinity of WPU film was analyzed by a Rigaku Ultima IV X-ray diffractometer (XRD). A scanning of 2θ angle was from 5 to 70°. The scanning speed was 0.1 s $step^{-1}$ and the every scanning step was 0.02°. The tensile strength and elongation at break of dumbbell-shaped splines (25 mm × 4 mm) were analyzed by using an electronic universal testing machine of Hegewald & Peschke at a tensile rate 100 mm $min^{-1}$ and room temperature. The contact angles (CAs) were determined using the DataPhysics OCA100 high speed video contact angle measurer. The water absorption test was to cut a completely dry WPU film into a 1 $cm^2$, weighed it, and recorded it as dry weight $W_0$. Soaked

it in distilled water at 25 °C for 24 h to test the water absorption. The mass after immersion was recorded as wet weight $W_1$. The water absorption W (%) was calculated according to the following formula: $W(\%) = (W_1-W_0)/W_0 \times 100\%$. The solid content was determined by taking a small amount of lotion into the mold, and then placed it in an oven at 60 °C for more than 24 h to weigh the sample in the mold. Finally, calculated the solid content M (%) using the following formula: $M(\%) = (M_1-M_2)/(M_1) \times 100\%$, where $M_1$ was the initial mass of lotion; $M_2$ was the mass after drying. The hardness of the WPU film was determined by the standard GB/T 6739-2006. The test method of WPU film adhesion is to first use a 250 μm applicator to coat WPU dispersion on PET film, and then test according to GB/T 9286-1998 after drying.

**Figures and Tables**

Before the continuous flow reaction, the feeding accuracy of the feed pump was tested. The raw materials in bottle 1 and bottle 2 were transported into the micromixer through pump 1 and pump 2 respectively for mixing. The mixed liquid at the outlet of the micromixer was collected for toluene dibutylamine titration test. The results are shown in Fig. S1. The test value of -NCO content in the mixed liquid is 10.27 %, which is close to the theoretical value of 10.31 % of the mixed liquid. Therefore, it can be considered that the feed ratio of the feed pump before entering the microreactor for reaction is accurate.

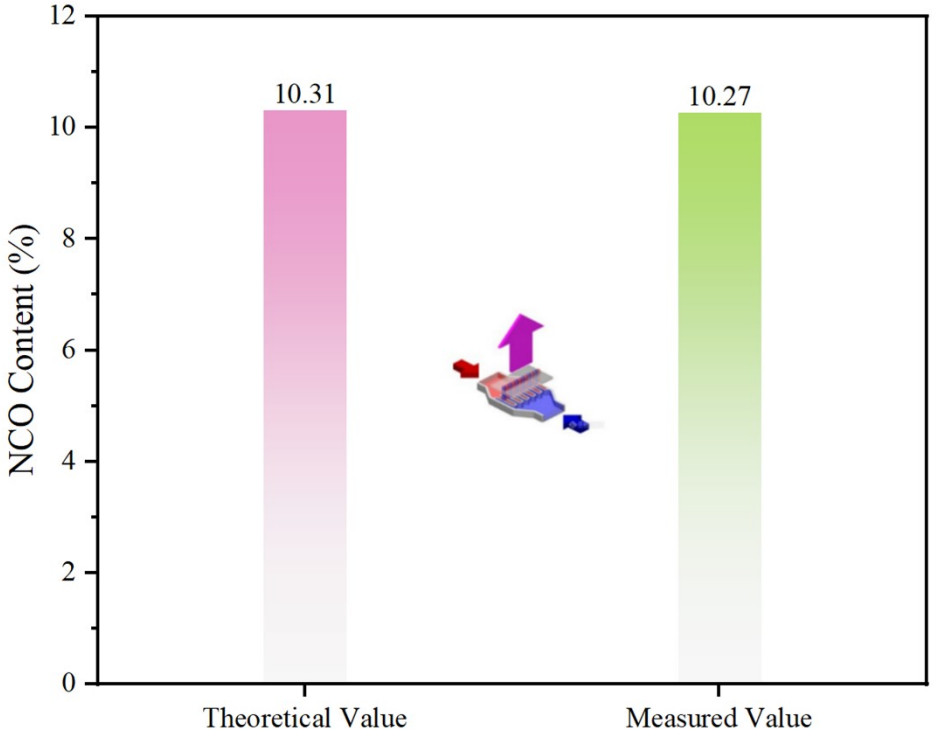


Fig. S1 Comparison of theoretical value and test value of -NCO content in the mixture at the outlet of micromixer.

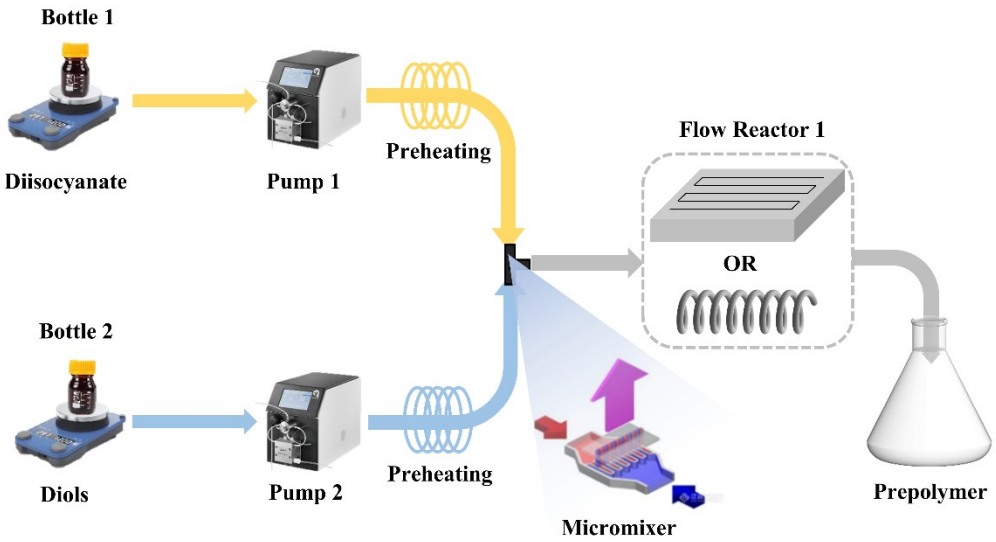


Fig. S2 Schematic diagram of prepolymer collection at the outlet of flow reactor 1.

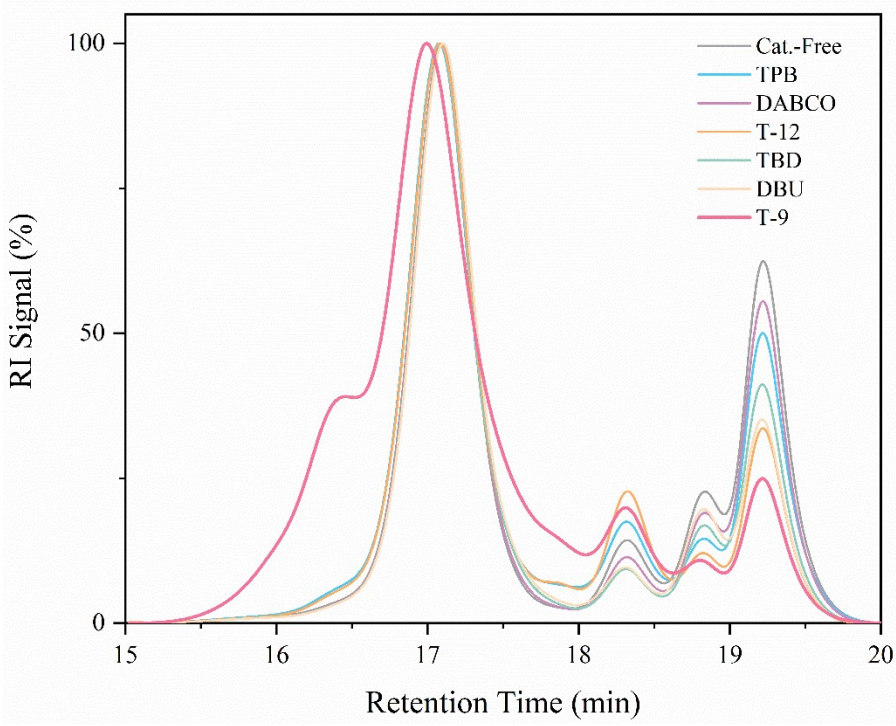


Fig. S3 The GPC curve of polyurethane prepolymer prepared under different kinds of catalysts

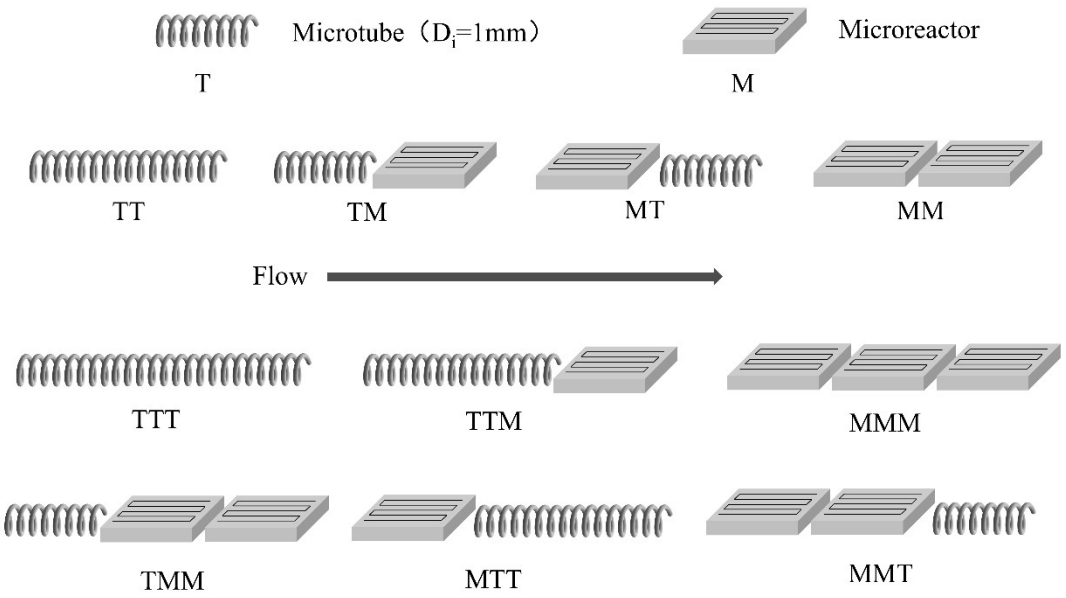


Fig. S4 Schematic diagram of different reactor configuration of microtube reactor and microreactor.

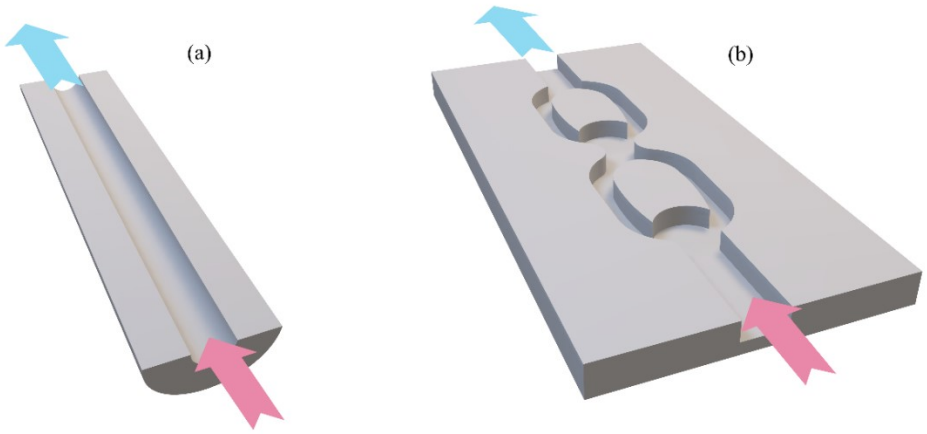


Fig. S5 Microtube reactor (a) and microreactor (b) cross section diagrams.

Table S1 Raw material ratio of batch reaction process

| IPDI (g) | PPG (g) | DMPA (g) | BDO (g) | DMF (g) | TEA (g) | $N_2H_4 \cdot H_2O$ (g) | $H_2O$ (g) |
|---|---|---|---|---|---|---|---|
| 21.84 | 40.00 | 3.33 | 1.49 | 13.33 | 2.51 | 1.38 | 144.00 |

Table S2 Experimental conditions of flow reactor 1 at different DMF dosage

| DMF (wt%) | DMF (g) | NCO (ml $min^{-1}$) | OH (ml $min^{-1}$) | $\tau_1$ (s) | $T_1$ (°C) | Cat. (wt%) | Flow Reactor |
|---|---|---|---|---|---|---|---|
| 15 | 10.00 | 1.488 | 3.927 | 43.5 | 150 | 0.25 | Microtube reactor |
| 20 | 13.33 | 1.420 | 4.000 | | | | |
| 25 | 16.67 | 1.358 | 4.054 | | | | |
| 30 | 20.00 | 1.302 | 4.112 | | | | |
| 35 | 23.33 | 1.250 | 4.164 | | | | |
| 40 | 26.67 | 1.202 | 4.213 | | | | |

*T-9 was used as catalyst in this experiment

Table S3 Experimental conditions of flow reactor 1 under different kinds of catalysts

| Cat. Type | DMF (g) | NCO (ml $min^{-1}$) | OH (ml/$min^{-1}$) | $\tau_1$ (s) | $T_1$ (°C) | Cat. (wt%) | Flow Reactor |
|---|---|---|---|---|---|---|---|
| Cat. Free<br>TPB<br>DABCO<br>T-12<br>TBD<br>DBU<br>T-9 | 13.33 | 1.420 | 4.000 | 43.5 | 100 & 150 | 0.25 | Microtube reactor & Microreactor |

Table S4 Experimental conditions of flow reactor 1 at different catalyst dosage

| Cat. (wt%) | NCO (ml min$^{-1}$) | OH (ml min$^{-1}$) | $\tau_1$ (s) | $T_1$ (°C) | Cat. Type | DMF (wt%) | Flow Reactor |
|---|---|---|---|---|---|---|---|
| 0 | 1.420 | 4.000 | 43.5 | 100 & 150 | T-9 | 20 | Microreactor |
| 0.05 | | | | | | | |
| 0.1 | | | | | | | |
| 0.15 | | | | | | | |
| 0.2 | | | | | | | |
| 0.25 | | | | | | | |
| 0.3 | | | | | | | |
| 0.35 | | | | | | | |
| 0.4 | | | | | | | |
| 0.45 | | | | | | | |
| 0.5 | | | | | | | |
| 0.75 | | | | | | | |
| 1 | | | | | | | |

Table S5 Experimental conditions of flow reactor 1 at different reaction temperatures

| T (°C) | NCO (ml min$^{-1}$) | OH (ml min$^{-1}$) | $\tau_1$ (s) | Cat. (wt%) | Cat. Type | DMF (wt%) | Flow Reactor |
|---|---|---|---|---|---|---|---|
| 100 | 1.420 | 4.000 | 43.5 | 0.25 | T-9 | 20 | Microreactor |
| 110 | | | | | | | |
| 120 | | | | | | | |
| 130 | | | | | | | |
| 140 | | | | | | | |
| 150 | | | | | | | |
| 160 | | | | | | | |
| 170 | | | | | | | |
| 180 | | | | | | | |

Table S6 Experimental conditions of flow reactor 1 at different residence times

| $\tau_1$ (s) | NCO (ml min$^{-1}$) | OH (ml/min$^{-1}$) | $T_1$ (°C) | Cat. (wt%) | Cat. Type | DMF (wt%) | Flow Reactor |
|---|---|---|---|---|---|---|---|
| 43.5 | 1.420 | 4.000 | 150 | 0.25 | T-9 | 20 | Microreactor |
| 87 | | | | | | | |
| 130 | | | | | | | |
| 174 | | | | | | | |
| 65 | 0.950 | 2.649 | | | | | |
| 130 | | | | | | | |
| 196 | | | | | | | |
| 262 | | | | | | | |

Table S7 Experimental conditions of flow reactor 1 at different total flow rates

| Vt (ml min$^{-1}$) | NCO (ml min$^{-1}$) | OH (ml min$^{-1}$) | $\tau_1$ (s) | Cat. (wt%) | Cat. Type | DMF (wt%) | Flow Reactor |
|---|---|---|---|---|---|---|---|
| 2.707 | 0.710 | 1.997 | 87 | 0.25 | T-9 | 20 | Microreactor |
| 5.420 | 1.420 | 4.000 | | | | | |
| 8.120 | 2.130 | 5.990 | | | | | |
| 10.827 | 2.840 | 7.987 | | | | | |
| 1.811 | 0.475 | 1.336 | 130 | | | | |
| 3.622 | 0.950 | 2.672 | | | | | |
| 5.420 | 1.420 | 4.000 | | | | | |
| 7.243 | 1.900 | 5.343 | | | | | |
| 1.353 | 0.355 | 0.998 | 174 | | | | |
| 2.707 | 0.710 | 1.997 | | | | | |
| 4.060 | 1.065 | 2.995 | | | | | |
| 5.420 | 1.420 | 4.000 | | | | | |

Table S8 Experimental conditions of flow reactor 1 under different types of reactor combinations

| | $\tau_1$ (s) | NCO (ml min$^{-1}$) | OH (ml min$^{-1}$) | Cat. (wt%) | Cat. Type | DMF (wt%) | Flow Reactor |
|---|---|---|---|---|---|---|---|
| T<br>M | 43.5 | 1.420 | 4.000 | 0.25 | T-9 | 20 | Microreactor & Microtube reactor |
| TT<br>TM<br>MT<br>MM | 87.0 | | | | | | |
| TTT<br>TTM<br>TMM<br>MTT<br>MMT<br>MMM | 130.0 | | | | | | |

Table S9 Experimental conditions of flow reactor 2 at different neutralization temperatures

| $T_2$ (°C) | NCO (ml min$^{-1}$) | OH (ml min$^{-1}$) | TEA (ml min$^{-1}$) | $\tau_2$ (s) | Flow Reactor |
|---|---|---|---|---|---|
| 90<br>100<br>110<br>120<br>130 | 1.420 | 4.000 | 0.238 | 42.0 | Microreactor |

Table S10 Experimental conditions of flow reactor 2 at different neutralization residence times

| $\tau_2$ | NCO | OH | TEA | $T_2$ | Flow Reactor |
|---|---|---|---|---|---|

| (s) | (ml min$^{-1}$) | (ml min$^{-1}$) | (ml min$^{-1}$) | (°C) | |
|---|---|---|---|---|---|
| 42.0<br>83.0<br>125.0 | 1.420 | 4.000 | 0.238 | 120 | Microreactor |

Table S11 Content of each raw material in each bottle in continuous flow process

| Bottle | IPDI (g) | PPG (g) | DMPA (g) | BDO (g) | DMF (g) | TEA (g) | $N_2H_4·H_2O$ (g) | $H_2O$ (g) |
|---|---|---|---|---|---|---|---|---|
| 1 | 21.84 | | | | | | | |
| 2 | | 40.00 | 3.33 | 1.49 | 13.33 | | | |
| 3 | | | | | | 2.51 | | |
| 4 | | | | | | | | 117.18 |
| 5 | | | | | | | 1.38 | 12.42 |
| Bucket | | | | | | | | 14.40 |

Table S12 Parameters of each feed pump when preparing M-WPU by continuous flow process

| Pump 1 (ml min$^{-1}$) | Pump 2 (ml min$^{-1}$) | Pump 3 (ml min$^{-1}$) | Pump 4 (ml min$^{-1}$) | Pump 5 (ml min$^{-1}$) |
|---|---|---|---|---|
| 1.420 | 4.000 | 0.238 | 8.085 | 0.952 |

Table S13 Experimental parameters of continuous flow process for preparing M-WPU

| $T_1$ (°C) | $\tau_1$ (s) | $T_2$ (°C) | $\tau_2$ (s) | DMF (wt%) | Cat. Type | Cat. (wt%) | Flow Reactor |
|---|---|---|---|---|---|---|---|
| 150 | 130.0 | 120 | 83.0 | 20 | T-9 | 0.25 | $F_1$: TMM<br>$F_2$: MM |

*$F_1$: Flow Reactor 1; $F_2$: Flow Reactor 2