Supporting Information

Optical Tracking the Heterogeneous Solvent Diffusion Dynamics and

Swelling Kinetics in Single Polymer Microspheres

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S1. Schematic illustration of flow cell and heating device



Fig. S1 Schematic illustration of flow cell and heating devices. (A) Schematic illustration of flow cell. The microparticle sample was dispersed in the glass slide, and the PTFE cell was applied to hold swelling solution. (B) Schematic illustration of sample stage with heating device. The heating device includes a thermocouple and a heating cell, and the thermocouple is at the top of the interior of heating cell. The entire heating system covers the flow cell where the reaction occurs, and the temperature of heating cell is regulated by a temperature control switch.

S2. The solvent diffusion dynamics of single PMMA microspheres in different swelling solutions



Fig. S2 The solvent diffusion dynamics of single 5 μ m PMMA microspheres in different swelling solutions. The time-lapsed BF intensity profiles of single PMMA microspheres in different swelling solutions: MeOH (A), EtOH (B) and H₂O (C). The inset bright field images indicate the corresponding single PMMA microspheres. (D-F) The corresponding diameter variation of single PMMA microspheres in three swelling solutions. Orange lines reveal the smooth results.

S3. Standard deviation of typical single PMMA microsphere



Fig. S3 Relative standard deviation (SD) of typical single 5 μ m PMMA microsphere in H₂O is about 5.72 nm.

S4. The calculated edge change of several single PMMA microspheres



Fig. S4 The calculated edge change of single 5 μ m PMMA (above is a bright field image of the same batch of single-particle spheres) microspheres with the solvent concentrations of 15.0% dichloromethane (ethanol) solution, where the line is the result after smooth.





Fig. S5 Imaging the diffusion dynamics of single 5 μ m PMMA microspheres under different temperatures in ethanol solutions containing 5.0% dichloromethane. Snapshots of BF images for a single representative PMMA microsphere under 296 K (A) and 316 K (B). (C, D) The false-color line profiles versus time along the orange dotted line in A and green dotted line in B, respectively. The magnifying false-color figures of the upper region (E) and the bottom region (G) are plotted in C. The magnifying false-color figures of the upper region (F) and the bottom region (H) are plotted in D. (I, J) The single-particle diameter vairation of orange line in A and green line in B, respectively.



S6. Swelling characteristics determination of single PS microspheres with different solvent concentrations

Fig. S6 Swelling characteristics determination of single 5 μ m PS particles with different solvent concentrations. Histogram of the equilibrium time (A-C) and the single-particle diameter variation during swelling process (D-F) of individual PS microspheres in different solutions. The red lines are the Gaussian fitting results. The average swelling equilibrium times of single PS microspheres in ethanol solutions containing 15.0%, 12.5% and 10.0% dichloromethane are 6.49±1.20 s, 20.90±5.44 s and 43.81±18.36 s, the corresponding average diameter variations are 256.5±49.4 nm, 106.4±15.9 nm and 44.2±6.6 nm, respectively.

S7. Trajectory curves for single PS microspheres with different solvent concentrations



Fig. S7 Trajectory curves for single 5 μ m PS microspheres with different solvent concentrations. (A) The timelapsed BF intensity curves with different solvent concentrations containing 15.0%, 12.5% and 10.0% dichloromethane. The inset false-color image reveals single PS microsphere, and the red cycle indicates the optical spot for tracking. Scale bar: 1 μ m. (B-D) The corresponding trajectory curves of the optical bright spot center during swelling reaction in A.



S8. Swelling characteristics determination of single PS microspheres with different sizes

Fig. S8 Swelling characteristics determination of single PS microspheres with different sizes in ethanol solutions containing 15.0% dichloromethane. Histogram of the swelling equilibrium time (A-B) and the single-particle diameter variation during swelling process (C-D) with the initial diameter of 5 μ m and 7 μ m. The red lines are the Gaussian fitting results. The average equilibrium times of 5 μ m and 7 μ m PS microspheres are 14.97±4.15 s and 73.16±13.53 s, and the corresponding average diameter variations are 289.8±23.0 nm and 327.3±34.2 nm, respectively.

S9. Imaging the diffusion dynamics of single PS microspheres with different sizes



Fig. S9 Imaging the diffusion dynamics of single PS microspheres with different sizes in ethanol solutions containing 15.0% dichloromethane. Snapshots of BF images for single representative PS microspheres with 5 μ m (A) and 7 μ m (B). The false-color BF images (C) and (D) versus time of orange dot line in A and green dot line in B, respectively. The vertical coordinates of C and D represent the dot line in A and dot line in B, respectively. The zoom-in false-color images of the upper area-of-interest (ROI) (E) and the bottom ROI (G) in C. The zoom-in false-color images of the upper ROI (F) and the bottom ROI (H) in D. Scatter diagram of the calculation edge change of orange line (I) in A and green line (J) in B, where blue dots are experimental data and orange lines are the results after smooth.