

Supplementary Material (ESI) for Chemical Communications

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K⁺-Recognition Capsules with Squirting Release Mechanisms

Supplementary Material

Zhuang Liu, Li Liu, Xiao-Jie Ju,* Rui Xie, Bao Zhang, and Liang-Yin Chu*

School of Chemical Engineering, Sichuan University, Chengdu, Sichuan, 610065, China

E-mail: chuly@scu.edu.cn; juxiaojie@scu.edu.cn

Experimental Section

Materials: *N*-isopropylacrylamide (NIPAM, Kohjin) was purified by recrystallization with a hexane/acetone mixture (50/50, v/v). Perylenedicarboxylic acid bis(2-methylpropyl) ester (8G) and lumogen Red 300 (LR300) were used as oil-soluble fluorescent dyes, and fluorescein-5-isothiocyanate (FITC, Sigma-Aldrich) was used as water-soluble fluorescent dye. Benzo-15-crown-5-acrylamide (B₁₅C₅Am) was synthesized from Benzo-15-crown-5 (B₁₅C₅, Sigma-Aldrich) according to reported procedures.^[S1,S2] *N,N*-methylene-bis-acrylamide (MBA) was used as a crosslinker. 2,2-Dimethoxy-2-phenylacetophenone (BDK, Haining Paulyuan Dyestuffs, China) and 2,2'-azobis(2-amidinopropane dihydrochloride (V50, Qingdao Runxing Photoelectric Materials, China) were used as photo-initiators. Polyglycerol polyricinoleate (PGPR, Danisco) and Pluronic F127 (Sigma-Aldrich) were used as emulsifiers. Deionized (DI) water from a Millipore Milli-Q Plus system was used in the experiments.

Microfluidic Devices: The microfluidic devices were fabricated according to our published method.^[S3] Briefly, three cylindrical capillaries were used as injection, transition and collection tubes by aligning them coaxially inside square capillaries. The outer diameter of cylindrical capillaries and the inner dimension of square capillary tubes were all 1.0 mm. The inner diameters of injection, transition and collection tubes were 580, 250, and 450 μm, respectively. The ends of injection and transition tubes were tapered by a micropuller (Narishige, Japan) and then adjusted by a microforge (Narishige, Japan).

Fabrication and Characterization of Microcapsules: The microcapsules were polymerized by using O/W/O double emulsions as the templates, which were generated by the microfluidic devices. In the microfluidic preparation of O/W/O emulsions, soybean oil containing 3% (w/v) PGPR and 0.1% (w/v) 8G or LR300 was used as the inner oil phase, and soybean oil containing 5% (w/v) PGPR was used as the outer oil phase. For the middle aqueous phase, 4 ml DI water containing NIPAM (0.365 g, 3.2 mmol), B₁₅C₅Am (0.108 g, 0.32 mmol), and AAm (0.023 g, 0.32 mmol), MBA (0.005 g, 0.032 mmol), V50 (0.008 g), glycerin (0.28 g), and Pluronic F127 (0.032 g) was used typically. The ratios of B₁₅C₅Am and AAm were varied for comparison. The O/W/O emulsions are collected in excess oil phase containing 1% (w/v) BDK. The microcapsules were fabricated via UV-initiated polymerization in an ice bath. After polymerization, the microcapsules were isolated from surrounding oil by adding benzyl benzoate and DI water, and then washed with DI water for several times. FITC was used to label the poly(NIPAM-*co*-AAm-*co*-B₁₅C₅Am) capsule membranes.

The characterization of the chemical structure of microcapsules was carried out with Fourier transform infrared spectroscopy (FT-IR, IRprestige-21, Shimadzu, Japan). Before FT-IR measurements, the inner oil cores had been removed from the microcapsules by washing them repeatedly with isopropyl alcohol and deionized water, and the microcapsules had been freeze-dried. The FT-IR specimen was prepared by using KBr disc technique.

The volume phase transition behaviors of microcapsules with PNIPAM, poly(NIPAM-*co*-B₁₅C₅Am) and poly(NIPAM-*co*-AAm-*co*-B₁₅C₅Am) membranes were investigated by measuring the diameter changes of microcapsules in different solutions and at various temperatures. In this series of experiments, the inner oil cores had been removed from the microcapsules by washing them repeatedly with isopropyl alcohol before measurements. The microcapsules were separately immersed in DI water, KNO₃, NaNO₃, Ca(NO₃)₂ and mixed ion solutions in small glass baths with 1 cm inner diameter. The diameters of microcapsules were measured by taking photos using an optical microscope equipped with a thermostatic stage system (TS62, Instec) and a CCD camera.

To study the K⁺-recognition-responsive behaviors, the microcapsules were first equilibrated in DI water at a designed temperature according to the component of microcapsule membrane (*e.g.*, 27 °C for poly(NIPAM-*co*-B₁₅C₅Am) microcapsules, and 37 °C for poly(NIPAM-*co*-AAm-*co*-B₁₅C₅Am) microcapsules). Then, the surrounding DI water was rapidly replaced with 0.2 M K⁺ solution, which was also preheated at the same temperature. At the same time, the K⁺-recognition-responsive behaviors of microcapsules

were recorded by a confocal laser scanning microscope (CLSM) (SP5-II, Leica) equipped with a thermostatic stage system (TSA02i, Instec).

Componential Analyses of Microcapsules

Fig. S3 shows FT-IR spectra of PNIPAM, poly(NIPAM-*co*-B₁₅C₅Am) and poly(NIPAM-*co*-AAm-*co*-B₁₅C₅Am) microcapsules. For the PNIPAM microcapsules, all the characteristic peaks of NIPAM are found including a strong peak at 1650 cm⁻¹ for C=O stretching vibration of the amidogroup and the characteristic double peaks at 1388 and 1368 cm⁻¹ for the isopropyl group. For the poly(NIPAM-*co*-B₁₅C₅Am) microcapsules, besides the characteristic peaks of NIPAM, the characteristic peaks of B15C5Am are all found including a strong peak at 1518 cm⁻¹ for C=C skeletal stretching vibration of the phenyl ring, a peak at 1228 cm⁻¹ for C-O asymmetric stretching vibration in Ar-O-R, and a peak at 1055 cm⁻¹ for C-O symmetric stretching vibration in Ar-O-R. For the poly(NIPAM-*co*-AAm-*co*-B₁₅C₅Am) microcapsules, all the characteristic peaks of NIPAM and B15C5Am are also found; however, the characteristic peaks at 1388 and 1368 cm⁻¹ for isopropyl group are relatively lower than those in the spectrum of poly(NIPAM-*co*-B₁₅C₅Am) microcapsules because of the introduction of AAm groups. The results confirm successful fabrications of all the microcapsules with PNIPAM, poly(NIPAM-*co*-B₁₅C₅Am) and poly(NIPAM-*co*-AAm-*co*-B₁₅C₅Am) membranes.

References

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- [S3] L. Y. Chu, A. S. Utada, R. K. Shah, J. W. Kim, D. A. Weitz, *Angew. Chem. Int. Edit.* **2007**, *46*, 8970.

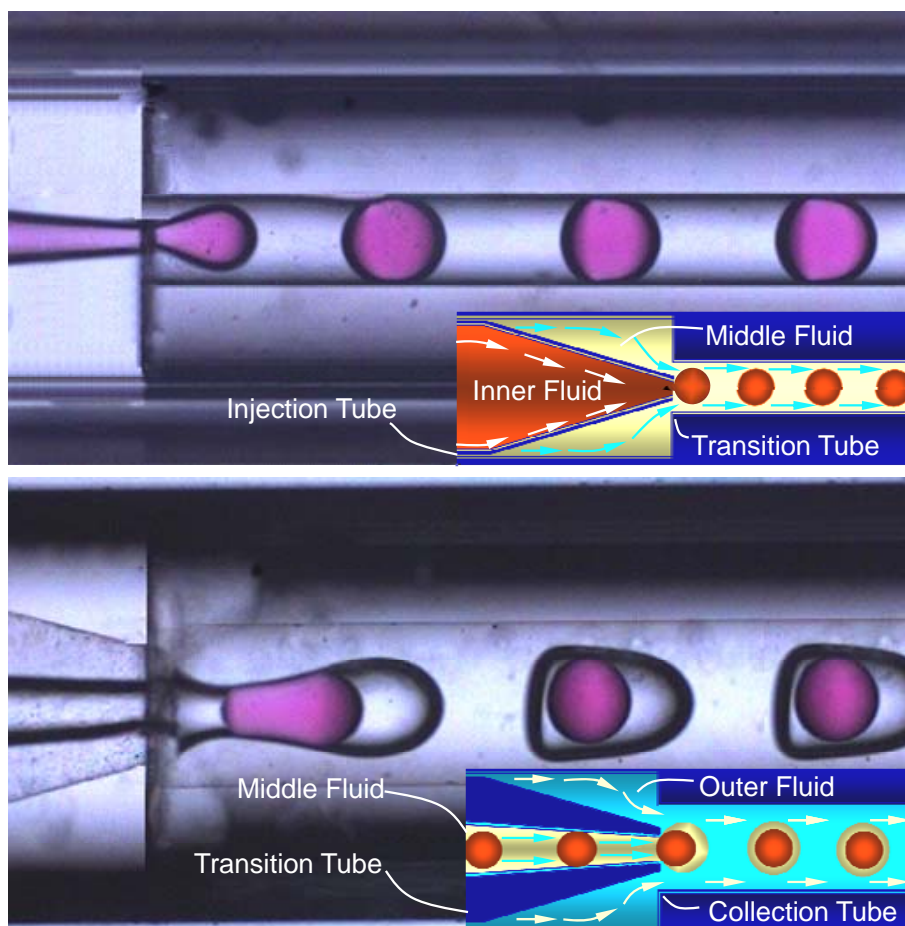


Fig. S1 Microfluidic fabrication of O/W/O double emulsions. The inner diameters of the ends of injection and transition tubes are approximately 80 and 200 μm respectively. The inner diameter of collection tube is about 450 μm . The flow rates of inner, middle and outer fluids are 600, 900 and 2700 $\mu\text{L}\cdot\text{h}^{-1}$, respectively.

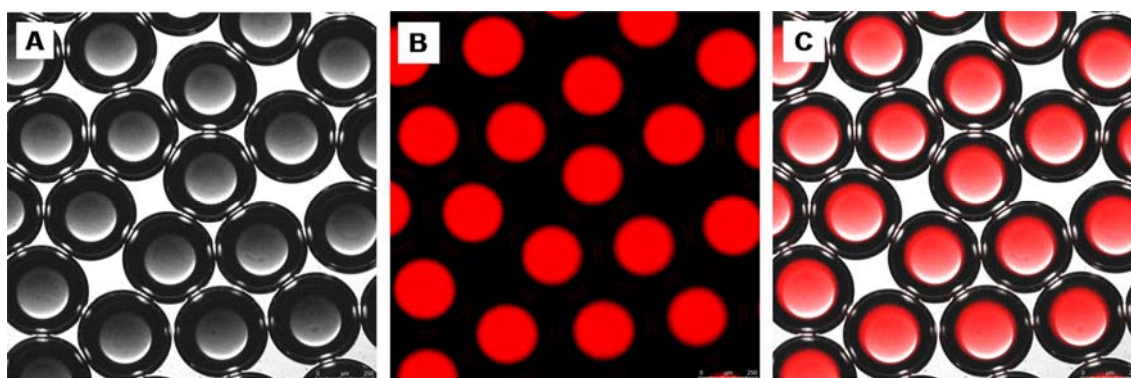


Fig. S2 CLSM images of monodisperse O/W/O emulsions with fluorescent dye LR300 in the inner oil phase. (A) Transmission channel image, (B) red channel image, and (C) overlay of red channel and transmission channel images. The scale bar is 250 μm .

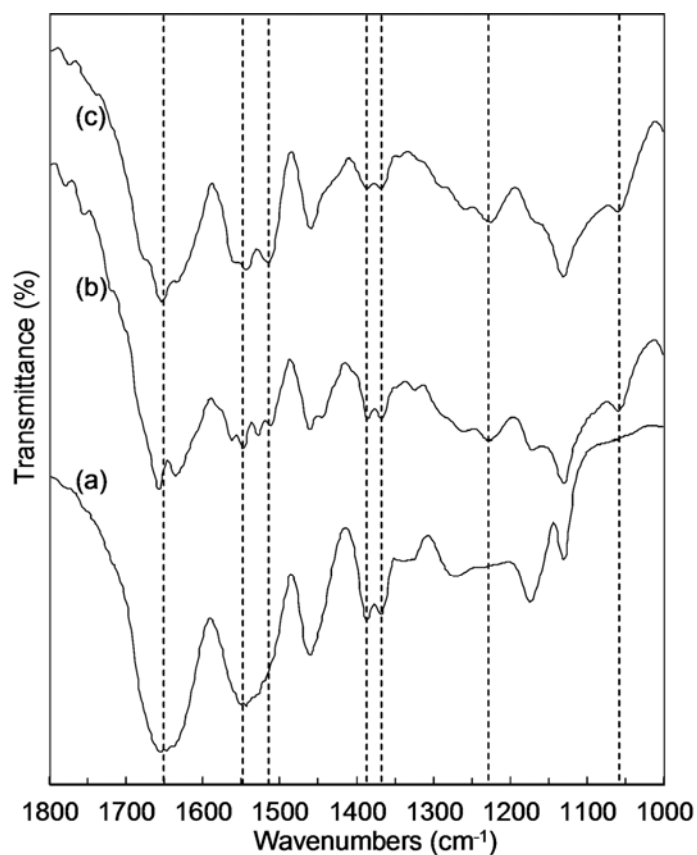


Fig. S3 FT-IR spectra of a) PNIPAM microcapsules, b) poly(NIPAM-*co*-B₁₅C₅Am) microcapsules with the molar ratio of B₁₅C₅Am to NIPAM being 10%, and c) poly(NIPAM-*co*-AAm-*co*-B₁₅C₅Am) microcapsules with the molar ratio of B₁₅C₅Am to NIPAM and that of AAm to NIPAM being both 10%.

Move S1. CLSM movie of K⁺-recognition-responsive squirting release behaviors of poly(NIPAM-*co*-B₁₅C₅Am) microcapsules.

Move S2. CLSM movie of K⁺-recognition-responsive squirting release behaviors of poly(NIPAM-*co*-AAm-*co*-B₁₅C₅Am) microcapsules.