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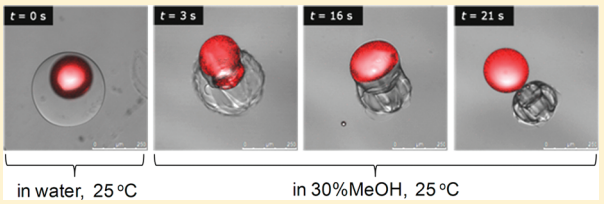
Conversion of Alcoholic Concentration Variations into Mechanical Force via Core−Shell Capsules

Li Liu, Xiao-Lu Song, Xiao-Jie Ju,* Rui Xie, Zhuang Liu, and Liang-Yin Chu*

School of Chemical Engineering, Sichuan University, Chengdu, Sichuan, 610065, P.R. China

Supporting Information

ABSTRACT: Conversion of chemical signals into mechanical force is very important for implementation of stimuli-responsive hydrogels. We design a core−shell hydrogel capsule that can translate the variations of alcohol concentration into mechanical force. Oil-in-water-in-oil (O/W/O) emulsions are prepared with microfluidic technique and serve as templates for the synthesis of the core−shell capsules. The oil core is ejected from the capsule by the mechanical force generated from the deswelling of the capsule membrane upon increasing the alcohol concentration at a certain temperature below the lower critical solution temperature. The influences of alcohol concentration and temperature on the deswelling process of capsule membranes are investigated systematically. The deswelling rate also plays an important role in the ejection of the oil core. These demonstrations of conversion of alcohol concentration variations into mechanical force provide proof that these core−shell capsules can function as both sensors and actuators of alcohols.



INTRODUCTION

Stimuli-responsive capsules have been considered as promising carriers in food, cosmetics, microreaction, and biomedical fields because they can change their structures and physical properties in response to external stimuli and would subsequently affect the release pattern from the reservoirs.[1−3] Poly(*N*-isopropylacrylamide) (PNIPAM), which exhibits a sharp lower critical solution temperature (LCST) around 32 °C, is one of the most extensively studied thermoresponsive materials. Cross-linked PNIPAM hydrogels (chemical structure shown in Figure 1A) swell below the LCST and deswell above the LCST. On the basis of the thermo-responsive phase transition properties, PNIPAM hydrogel materials have found various potential applications in controlled drug delivery, enzyme immobilization, cell culture, and medical and biological sensors.[4,5]

The nature of the thermoresponsive property of PNIPAM polymer is revealed as the balance between hydrogen bonding and hydrophobic interaction.[6] Solvents, which not only change the aqueous environment but also form hydrogen bonds with both water and PNIPAM molecules, can also induce the same phase transition.[7] So far, numerous studies have been conducted on the solvation behaviors of PNIPAM polymer in mixed solvents. Most of these works have focused on the coil-to-globule transition of linear PNIPAM polymers[6,8−10] or the volume transition of cross-linked PNIPAM macrogels.[11−13] The swelling behaviors of PNIPAM microgels[14−17] and even core−shell microgels[18] were also investigated. In a practical operating system, it demands not only a sensor but also an actuator.[19] It would be quite beneficial if the materials were to function as both sensor and actuator, in which case mechanical force generated from chemical signals is desired.[20−24] So far, all the previous studies have been trying to reveal the nature of this cononsolvency behavior, but none of them has attempted to translate this cononsolvency behavior into mechanical forces.

Alcohol is one of the most common solvent species for many scientific, medical, and industrial utilities. In organic synthesis, alcohols generally serve as versatile solvents whose concentration may have great effects on the reaction environment and, subsequently, the products. Ethanol in the form of alcoholic beverages has been consumed by humans since prehistoric times and may cause intoxication when a person has a high level of ethanol in his/her blood. Thus, it would make sense to take advantage of the alcohol-sensitivity of PNIPAM hydrogel to develop a capsule which can sense the variation of alcoholic concentration and convert the signal into mechanical forces.

Here, we design an alcohol-responsive PNIPAM capsule that can convert the variations of alcohol concentration into mechanical force, as demonstrated in Figure 1B. An oil core is encapsulated inside the PNIPAM capsule to demonstrate the generated mechanical force by ejecting the oil core from the capsule upon alcohol concentration variation. It has been reported that in water-rich solvents, water molecules form cage-like structures around the hydrophobic groups of PNIPAM polymer chains and form hydrogen bonds with the amide groups.[17] So the PNIPAM capsule membrane remains at a swollen state, and the oil core is completely encapsulated by the capsule membrane. When more alcohol is added, water and alcohol molecules form complexes because solvent−solvent interactions are favored. Therefore, a decrease in water molecules surrounding PNIPAM polymer chains results. As a consequence, a less solvated PNIPAM results.

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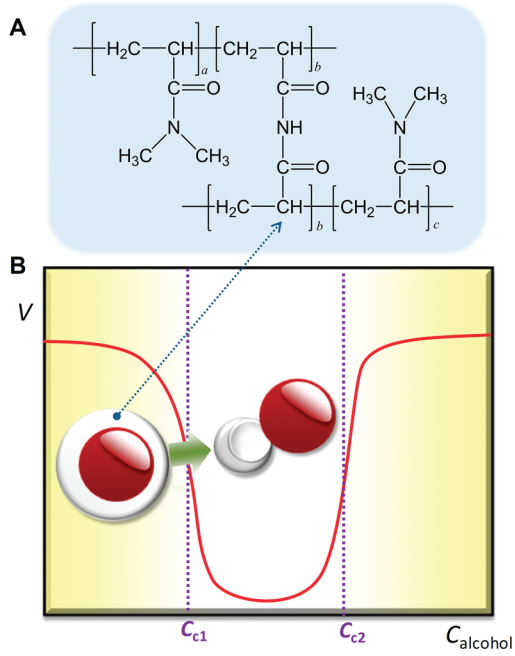

Figure 1. (A) Chemical structure of PNIPAM. (B) Schematic illustration of the concept of transition of solvent concentration variation into mechanical force.

In a certain alcohol concentration range ($C_{c1} < C < C_{c2}$, as shown in Figure 1B), all the water molecules previously solvating PNIPAM are bonded with alcohol molecules. This leads to a reduced solvency of PNIPAM with water, and therefore polymer−polymer interactions become dominant, and then, PNIPAM polymer chains turn into the collapsed state and the capsule membranes become shrunken.[9−11,13,16,17,25] Because the inner oil core is incompressible, such contraction action is hindered and the pressure inside the capsules increases dramatically. Eventually, the accumulated pressure turns into mechanical force to rupture the capsule membrane and eject the oil core into the environment.

The investigations are conducted in methanol and ethanol solutions. Schneider and Kato[26,27] defined that chemomechanical polymers have the unique feature of combining a sensor and an actuator with producing large and reversible motions upon exposure to chemical stimuli in the environment. The capsule presented in this paper can act as an actuator through ejection of the encapsulated oil core triggered by alcohol concentration variation. This ejection movement of the oil droplet is a perfect demonstration of mechanical energy. Furthermore, the oil core can either be an indicator itself or contain some kind of active substances that are involved in further reaction. In addition, the quick and complete release pattern triggered by alcohol offers a potential opportunity for cargo delivery in alcoholic environments.

EXPERIMENTAL SECTION

Microfluidic Device. The microfluidic device for fabrication of oil-in-water-in-oil (O/W/O) emulsions is assembled according to our previous method.[28−30] Briefly, three cylindrical capillaries are used as the injection, transition, and collection tubes by aligning them coaxially inside the square capillaries. The outer diameter of the cylindrical capillaries is 1.0 mm, and the inner dimension of the square capillary tubes is 1.0 mm. The inner diameters of the injection, transition, and collection tubes are 500, 200, and 550 μm, respectively. The ends of injection and transition tubes are tapered by a micropuller (Narishige, Japan) and then adjusted by a microforge (Narishige, Japan). The tapered orifice diameters of the injection and transition tubes are 60 and 150 μm, respectively.

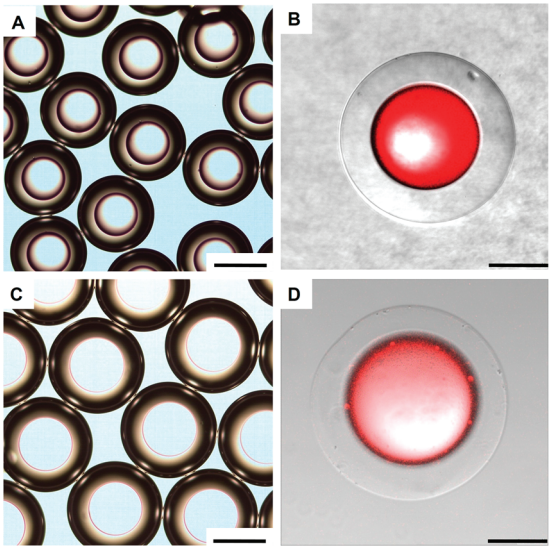

Figure 2. Optical images of the double emulsions containing soybean oil (A) and silicon oil (C) (scale bar = 200 μm), and CLSM images of the PNIPAM capsules containing soybean oil (B) and silicon oil (D) (scale bar = 100 μm).

Microfluidic Emulsification. The fluorescent dye Lumogen Red 300 is dissolved in soybean oil or silicon oil (1 mg/mL), which is used as the inner fluid. The middle fluid is monomer aqueous solution containing surfactant Pluronic F127 (1% (w/v), Sigma-Aldrich), monomer *N*-isopropylacrylamide (NIPAM) (1 mol L^{-1}, Kohjin), cross-linker *N*,*N*′-methylenebisacrylamide (MBA) (0.02 mol L^{-1}), and initiator 2,2′-azobis(2-amidinopropane) dihydrochloride) (0.005 mol L^{-1}). Soybean oil containing 8% (w/v) polyglycerol polyricinoleate (PGPR 90) is employed as the outer fluid. The inner, middle, and outer fluids are separately pumped into the injection, transition, and collection tubes of the microfluidic device. O/W/O emulsions generated in the collection tube are collected in soybean oil containing 2% (w/v) 2,2-dimethoxy-2-phenylacetophenone (BDK) as the photoinitiator.

UV-Initiated Polymerization. The collected O/W/O emulsions are converted into microcapsules via polymerization with UV irradiation for 10 min in an ice−water bath. A 250 W UV lamp with an illuminance spectrum of 250−450 nm is employed to produce UV light. The ice−water bath is introduced to ensure that the polymerization is carried out at temperature below the LCST of PNIPAM. Under UV light, the activated photoinitiator BDK diffuses to the interface between the outer oil phase and middle aqueous phase, where the polymerization of NIPAM monomer is initiated. The microcapsules are separated from the oil by adding benzyl benzoate into the container. After soybean oil and benzyl benzoate are completely mixed, deionized water is added. When the oil phase and water phase are completely separated, the capsules floating on the top surface of the water phase are collected. The microcapsules are washed with deionized water several times and then dispersed in deionized water.

Characterization. Optical microscope images are obtained by an Olympus optical microscope (BX 61). The LCST of PNIPAM

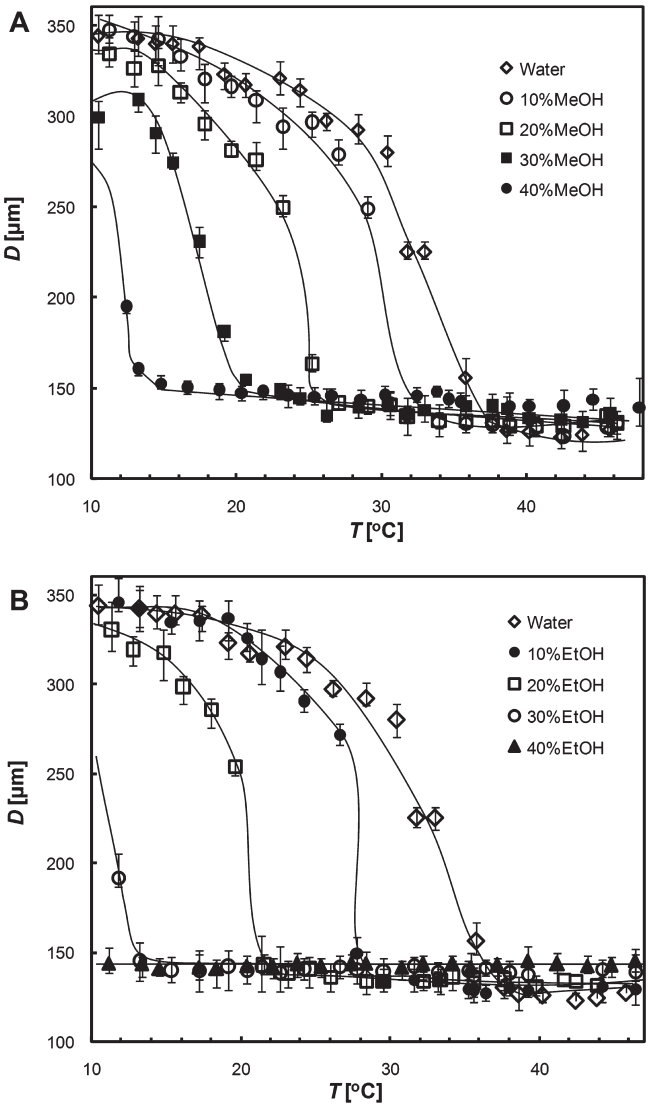

Figure 3. The sizes of hollow PNIPAM capsules as functions of the temperature in aqueous methanol solution (A) and aqueous ethanol solution (B).

capsules are determined by the optical microscope on the thermostatic stage system (TS 62, Instec, Boulder, CO, USA). The capsules are equilibrated at each temperature for 30 min, and the outer diameters of 10 capsules at each temperature are measured by analysis software. The dynamic volume transition process triggered by alcohol concentration change is also studied and recorded by a CCD camera mounted on the optical microscope. The capsules are immersed in deionized water at the preset temperature for 30 min. Then the water is removed, and alcohol solution that has been equilibrated at the same temperature is added. The deswelling ratio is calculated as V_t/V_0, in which V_t is the volume at the time t after adding alcohol and V_0 is the equilibrated volume in deionized water before adding alcohol. Fluorescent images of capsules and the ejection process are obtained by a confocal laser scanning microscope (CLSM) (Leica Microsystem SP5-II) equipped with a thermostatic stage (TSA02i, Instec). All the alcohol concentration mentioned in this paper is in the form of volume fraction.

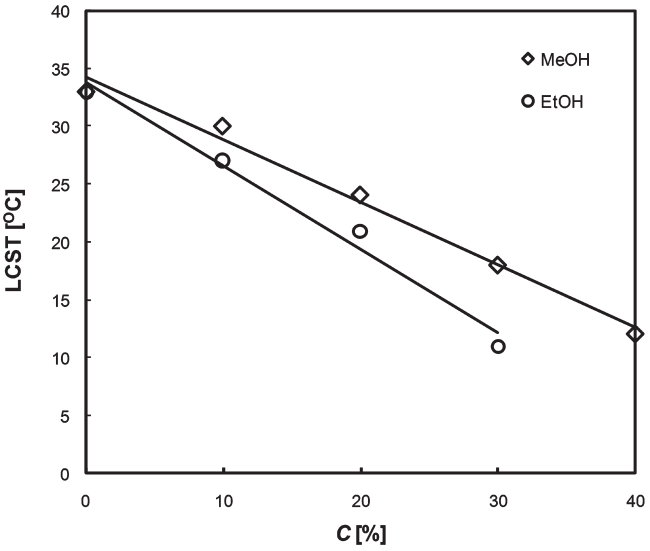

Figure 4. The LCSTs of hollow PNIPAM capsules as a function of alcoholic concentration.

RESULTS AND DISCUSSION

The optical images of the O/W/O double emulsions containing soybean oil core and silicon oil core are shown in Figure 2A and C, respectively. Using microfluidic technique, the number of oil cores can be precisely controlled. In this experiment, the number of inner oil cores is strictly limited to one so that the double emulsion templates can be converted into capsules with a core−shell structure. This structure allows the oil reservoir to be as large as possible to offer a better visualization of the mechanical force generated from the contraction of the PNIPAM hydrogel membrane. Soybean oil was chosen as the inner fluid first. However, we found that soybean oil is partially soluble in ethanol, even at low concentration so the oil core dissolves before being ejected out. Then silicon oil, which is less soluble in ethanol, was used as the inner fluid for ethanol-responsive experiment. From Figures 2A and 2C, we can see the double emulsions have monodisperse size and identical structure.

The CLSM images of the resultant PNIPAM capsules dispersed in water at room temperature are shown in Figure 2B and 2D. Because the environmental temperature is lower than the LCST, the hydrogel capsule membrane is transparent and swollen. However, the oil core cannot permeate through the hydrogel capsule membrane because the oil is totally insoluble in water.

Because of the incompressibility of the inner oil core, it would hinder the contraction of the hydrogel membrane (see Figure S1 in the Supporting Information). To investigate how the alcohol concentration influences the LCST of the PNIPAM capsules, the oil cores of the PNIPAM capsules are removed with isopropyl alcohol, and the capsules are washed repeatedly with deionized water, so the real size change of the PNIPAM capsules can be exactly measured without the influence of the oil cores. The size variations of the hollow capsules with temperature change in aqueous alcoholic solutions have been investigated systematically on a thermostatic stage under a microscope.

The temperature-dependence of the size of the hollow capsule in aqueous alcoholic solutions is shown in Figure 3. The PNIPAM capsules exhibit different LCSTs in aqueous solutions with different alcohol concentrations. No matter whether they

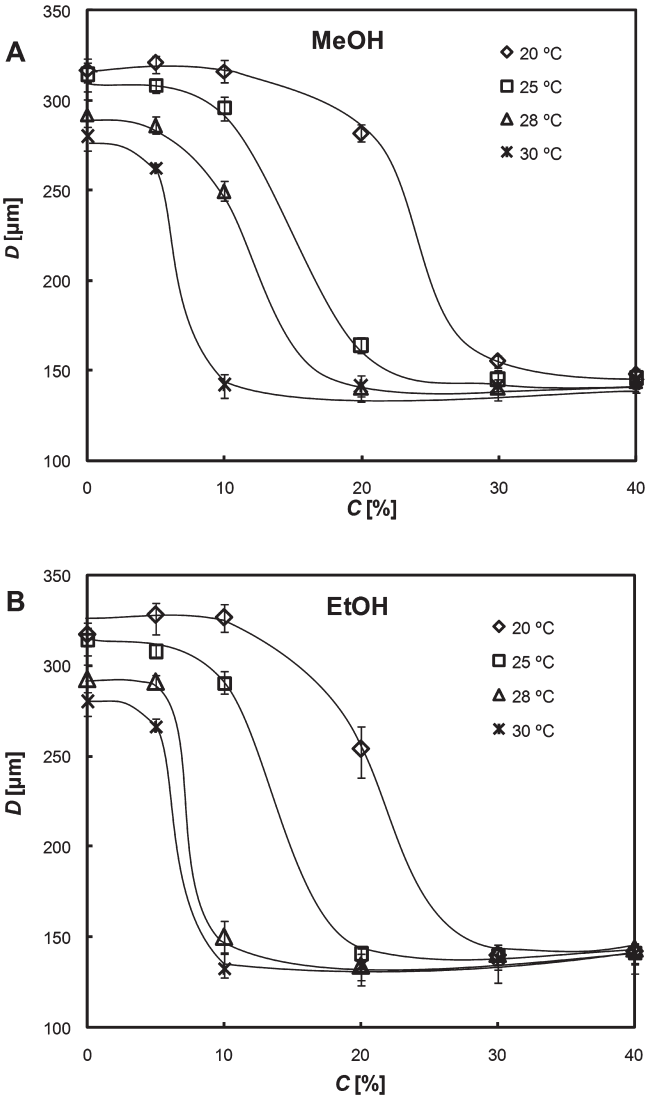

Figure 5. The sizes of hollow PNIPAM capsules as functions of the alcoholic concentration in aqueous methanol solution (A) and aqueous ethanol solution (B).

are in a methanol solution or in an ethanol solution, the LCST shifts of PNIPAM capsules show similar trends. The higher the alcohol concentration is, the lower the LCST shifts to. The LCSTs of PNIPAM capsules decrease linearly with an increase in the alcohol concentration (Figure 4). In addition, ethanol has a stronger dehydration ability than methanol at the same concentration and same temperature, which is consistent with previous studies.[7] It has been reported that a sharper decrease in the PNIPAM microgel size as the number of carbon atoms in the alcohols increases in the water-rich region and the minimum size of PNIPAM microgels that can be achieved is smaller than that in methanol.

In practical use, it is usually demanded that the systems perform isothermally at room temperature. It can be seen from Figure 4 that LCSTs of PNIPAM microcapsules range from 12 to 33 °C. The size variations of PNIPAM capsules with a change in alcohol concentration at 20, 25, 28, and 30 °C are plotted in Figure 5. In the alcohol concentration range from 0 to 40%, the PNIPAM capsules change from a swollen state to a shrunk state.

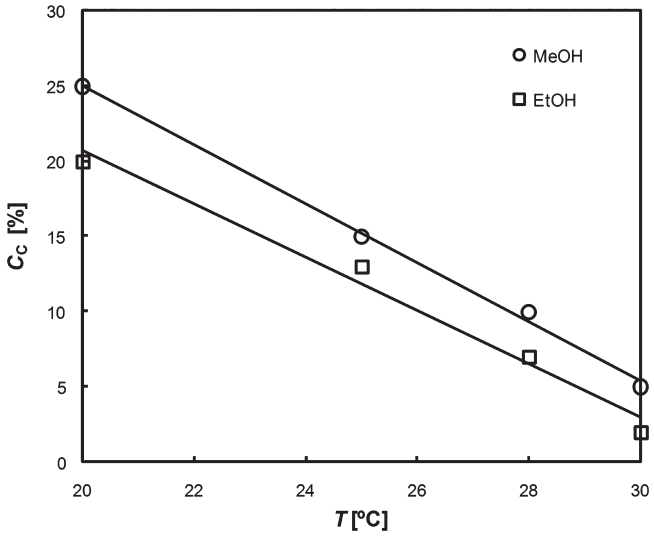

Figure 6. The C_c values of hollow PNIPAM capsules as a function of temperature.

In the temperature range adopted in this experiment, the PNIPAM capsules reach their minimum size at 40% methanol concentration or at 30% ethanol concentration. The minimum sizes of PNIPAM capsules are almost identical when dehydrated by the same alcohol species, which means no more water molecules remain surrounding the PNIPAM chain to interact with alcohol molecules at those alcohol concentrations. In addition, the minimum size of the PNIPAM capsules is slightly smaller in ethanol than that in methanol, as described above.

The alcoholic critical concentration (C_c) values where the isothermal volume phase transition occurs are plotted in Figure 6. The C_c values decrease linearly with increasing temperature, which indicates that the higher the operation temperature is, the lower the alcoholic critical concentration required for triggering the isothermal volume phase transition. The C_c values of ethanol solution are lower than those of methanol solution at the same temperature. In previous studies, it has been reported that the required concentration of alcohol solution for PNIPAM polymer to reach the minimum size shifts to a lower value as the number of carbon atoms in alcohols increases.[4,9,14] So does the C_c value in this work. The alcohols with more carbon atoms have stronger dehydration capacity than those with fewer carbon atoms. The lower C_c value can be explained in that the more carbon atoms present, and the more water molecules are required to form a clathrate structure around the alcohol molecules. As a consequence, the more water molecules around the PNIPAM chains are deprived by alcohol molecules.

The response rate is also an important factor for actuators. So the deswelling dynamics of the PNIPAM capsules in alcohol solutions at room temperature are also investigated in this work. Figure 7 shows the time-dependent deswelling ratio of PNIPAM capsules in alcoholic solutions. Generally, the higher the alcohol concentration is, the faster the PNIPAM capsules deswell. In fact, the deswelling rate plays an important role in the ejection action of the oil core. It has been reported that the thermosensitive hydrogels form a dense skin layer during the dehydration process.[31−33] The formation of the skin layer makes the capsule membrane hard to break. If PNIPAM capsules cannot reach a size small enough to generate enough mechanical force to rupture the

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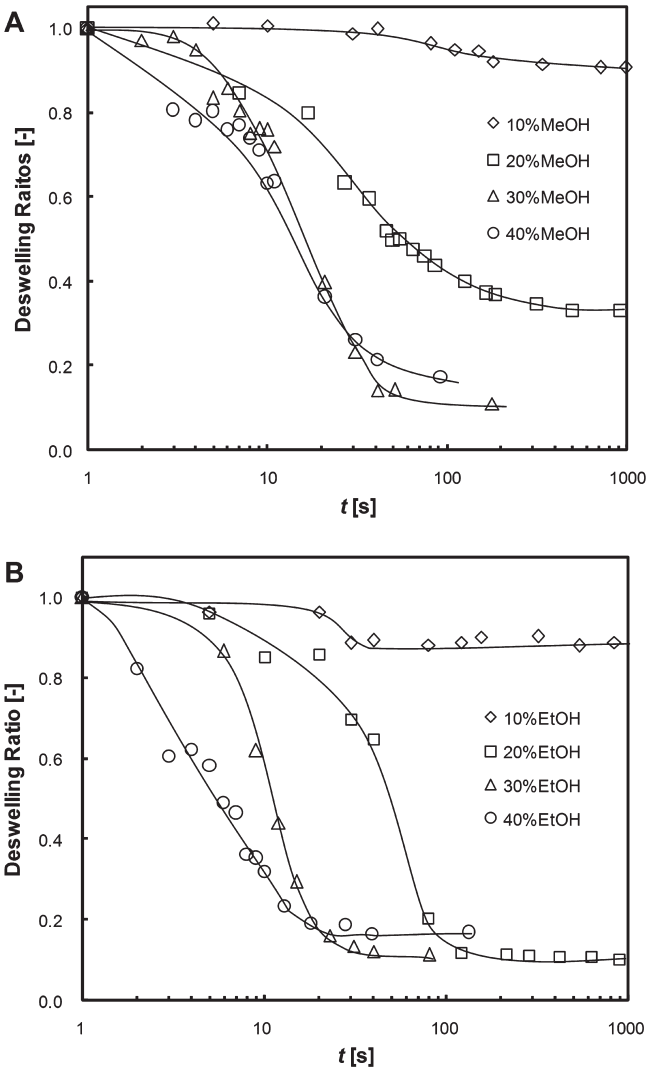

Figure 7. Deswelling ratios of hollow PNIPAM capsules as functions of time in aqueous methanol solution (A) and ethanol solution (B) at 25 °C.

membrane before the formation of the skin layer, the PNIPAM capsules will never break. Although the size of the PNIPAM capsules can shrink to nearly their minimum sizes in 20% methanol solution at 25 °C (Figure 5), it is found that the core−shell microcapsules fail to eject the oil cores at such alcohol concentration and temperature because the PNIPAM capsules shrink too slowly under such conditions (Figure 7A). In contrast, the PNIPAM capsules shrink to their minimum sizes within 40 s or even a shorter time in alcoholic solution with 30% or 40% alcohol concentration at 25 °C.

Figure 8 shows some perfect examples of such conversion of alcohol concentration variations into mechanical forces to eject the oil cores (see the Supporting Information for movies S1 and S2 to show the processes). At 25 °C, the PNIPAM capsules are completely swollen in deionized water first. Then, all the environmental deionized water is removed and alcohol solution with a certain concentration at the same temperature is added to the environment of the capsules.

The thickness of the prepared hydrogel membrane usually is not perfectly uniform, as seen in Figure 8. This difference in membrane thickness results from the density difference between

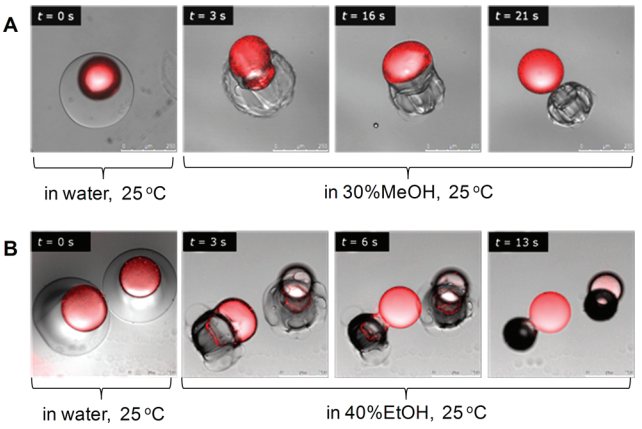

Figure 8. Snapshots of the burst release process of oil cores from PNIPAM capsules upon adding 30% methanol (A) and 40% ethanol (B) at 25 °C. The PNIPAM capsules are in pure water at $t = 0$ s. Scale bar = 250 μm.

the inner oil phase and the middle monomer solution in the O/W/O emulsion. The encapsulated oil phase is not usually in the exact center of the O/W/O emulsion droplet. Consequently, the oil core in the hydrogel capsule is not in the exact center, neither. Therefore, the thickness of the polymerized hydrogel membrane is not uniform, but a little thicker on one side and a little thinner on the other side. Sometimes, the oil core of the microcapsule appears to be in the center (Figures 2B, D) because the thinner side of the hydrogel membrane is either just right at the top or at the bottom. Since the microscope objective is vertical to the sample container, the oil core appears in the center of the microcapsule. As the dehydration in the PNIPAM capsule membranes goes on, the capsule membranes shrink rapidly, and the oil cores are pushed aside. Eventually, the PNIPAM capsules shrink to the size that cannot provide enough space to trap the oil cores inside anymore, so the hydrogel capsule membranes rupture and eject the inner oil cores. These examples give demonstrations that the alcohol concentration variation can be converted into mechanical force via our presented core−shell PNIPAM capsules.

CONCLUSIONS

Demonstrations of conversions of the alcohol concentration variation into mechanical force are given in this paper using core−shell PNIPAM capsules. O/W/O emulsions, which are prepared with microfluidic emulsification techniques, are used as templates for synthesizing the core−shell capsules by polymerizing the middle monomer water phase into the PNIPAM capsule membrane. Mechanical force is generated from the deswelling of the PNIPAM capsule membranes upon adding alcohols. The influences of alcohol concentration and temperature on the deswelling properties of PNIPAM capsules are investigated systematically. Generally, the critical concentration in the water-rich region decreases with increasing temperature. The deswelling dynamics of PNIPAM capsules at 25 °C were also investigated because it plays an important role in the membrane shrinkage and the ejection of the oil cores. The higher the alcohol concentration, the faster the hydrogel capsule deswells, and then the easier the capsule membrane breaks. The proposed concept of conversion of the alcohol concentration variation into mechanic force proves that core−shell PNIPAM capsules can function as both sensors and actuators of alcohol, which may also provide opportunities in cargo delivery in alcoholic environments.

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■ ASSOCIATED CONTENT

Supporting Information. Figure S1 for size variation with time after adding 30% methanol at 25 °C for core−shell and hollow PNIPAM capsules; movies S1 and S2 to show the processes of conversion of alcohol concentration variations into mechanical forces to eject the oil cores corresponding to Figure 8. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone, Fax: +86 28 8546 0682. E-mail: chuly@scu.edu.cn (L.-Y.C.); juxiaojie@scu.edu.cn (X.-J.J.).

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