Supplementary Material (ESI) for Chemical Communications

Manuscript title:

A totally synthetic glucose responsive gel operating in physiological aqueous conditions

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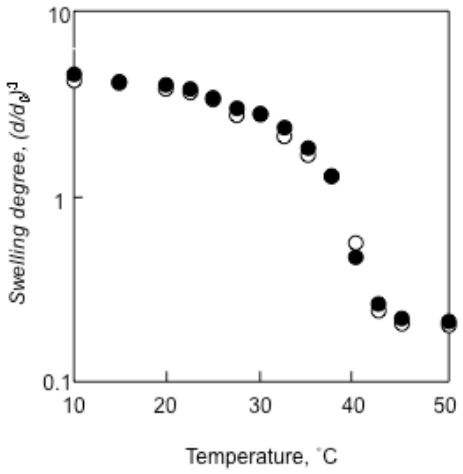
Detailed Method

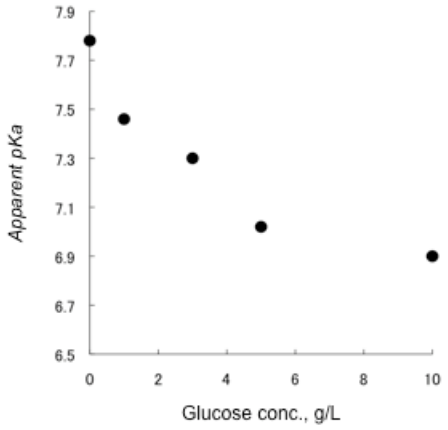
Materials. N-isopropylmethacrylamide (NIPMAAm) was synthesized by reacting methacryloyl chloride (Wako, Japan) with isopropylamine (Wako, Japan) through an identical procedure that has been reported previously[5 (b),7], which was then recrystallized in a 20/80 mixture of toluene and hexane. 4-(1,6-Dioxo-2,5-diaza-7-oxamyl) phenylboronic acid (DDOPBA) was synthesized by a two-step reaction as has been previously described.[7] 2-Carboxyisopropylacrylamide (CIPAAm) was synthesized in the same manner as previously reported by Aoyagi et al.[8] 2,2'-Azobisisobutyronitrile (AIBN) (Wako, Japan) was recrystallized from methanol. A cross-linker N, N'-methylene-bis-acrylamide (MBAAm) (Wako, Japan) and dimethylsulfoxide (Wako, Japan) were utilized as received.

Preparation of capillary gels and observation of glucose-responsive volume changes. Capillary (cylindrical) gels were prepared by radical copolymerization in 1 mm-diameter glass capillaries using 2,2'-azobisisobutyronitrile (AIBN) as an initiator, and in the presence of N, N'-methylene-bis-acrylamide (MBAAm) as a crosslinking agent. The concentrations of total monomer, AIBN and MBAAm in feed were 1.5 M, 7.5 mM and 30 mM, respectively. The reactions were allowed at 60˚C for 24h. The obtained gels were taken out of the capillaries and washed with an excess amount of distilled water to thoroughly exchange the solvent from DMSO to water and to remove any unreacted reagents. Diameter changes of the capillary gels were observed under a microscope (NIKON, DIAPHOT) equipped with a black-white CCD camera (HAMAMATSU photonics, C2400). The obtained images were processed through analytical software (HAMAMATSU photonics, IMAGE PROCESSOR ARGUS C5510) and then recorded by a video recorder. For the temperature control while observing the gels, a water-flow chamber of transparent acrylic resin with cavities on top was placed on the microscope

stage. The gel capillaries that were cut into 5 mm long (on shrunk state) pieces were placed in the cavities filled with each experimental buffer solution. The equilibrium volume changes upon decreasing the temperature were recorded for various glucose concentrations to obtain the phase diagrams. Assuming symmetric shape changes of the gels, the swelling degree was defined as $(d/d_0)^3$, where d_0 is the diameter as obtained in a glass capillary (1 mm for all in DMSO), and d is the observed diameter.



ESI Figure 1. Phase diagrams of poly(NIPMAAm) gel with (5 g/L: fixed circles) and without (opened circles) glucose investigated in a pH7.4 PBS.



ESI Figure 2. Glucose-dependent change in the apparent pKa value of DDOPBA at 25˚C as determined by potentiometric titrations.