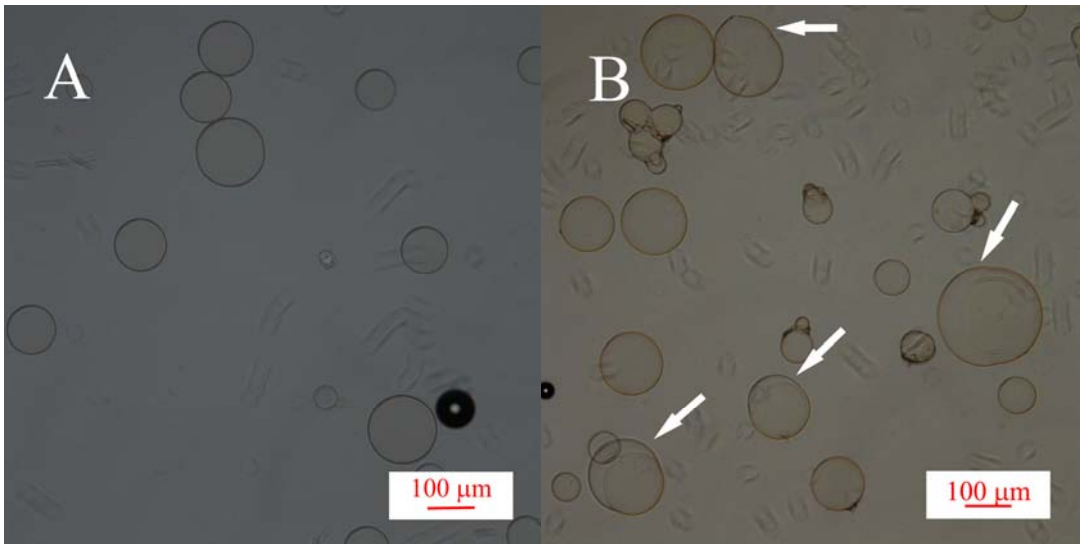

Figure S1. Optical micrographs of (A) Agarose microbeads coated with 2 bi-layers of (niPA/niPAA) in ethanol (B) Agarose microbeads coated with 2 bi-layers of (niPA/niPAA) in 50% ethanol 50% 5mg mL^{-1} PAH in 0.05x PBS. Detachment of LbL capsular walls from some agarose microbeads was observed (white arrows).

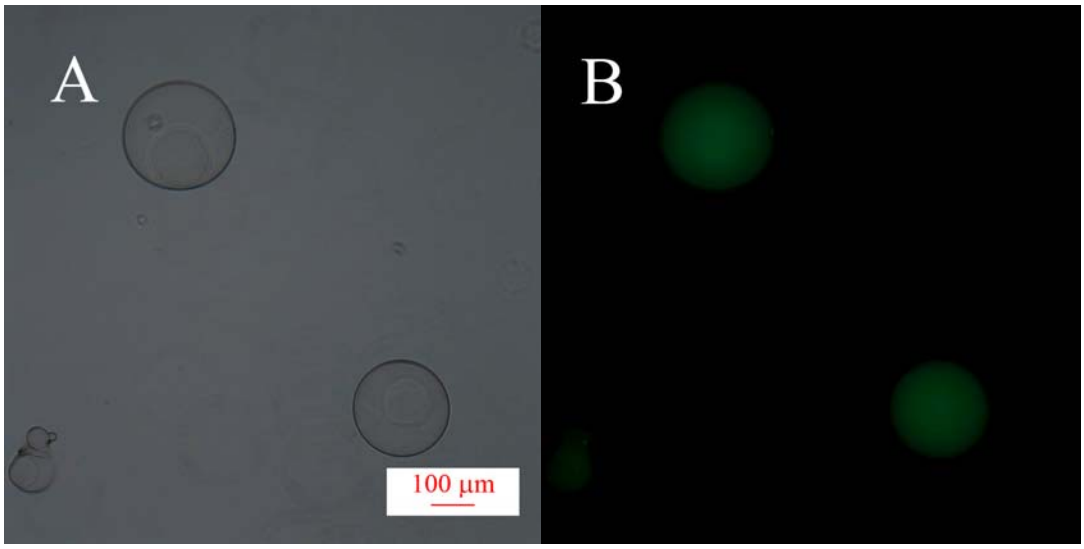

Figure S2. (A) Optical and (B) fluorescence micrographs of inflated microcapsules coated with 2 bilayers of (niPA/niPAA) and encapsulating dextran-FITC (2,000,000). The microcapsules were imaged as soon as possible (<5 minutes) after transferring into an aqueous phase. Inflation of >90% was observed and the fluorescence from dextran-FITC within its internal core was observed to be evenly distributed. This demonstrates that the inflation of LbL capsular walls occurs within minutes and that the agarose microbeads have poor retention capability for dextran with molecular weight up till at least 2,000,000 Da.

.

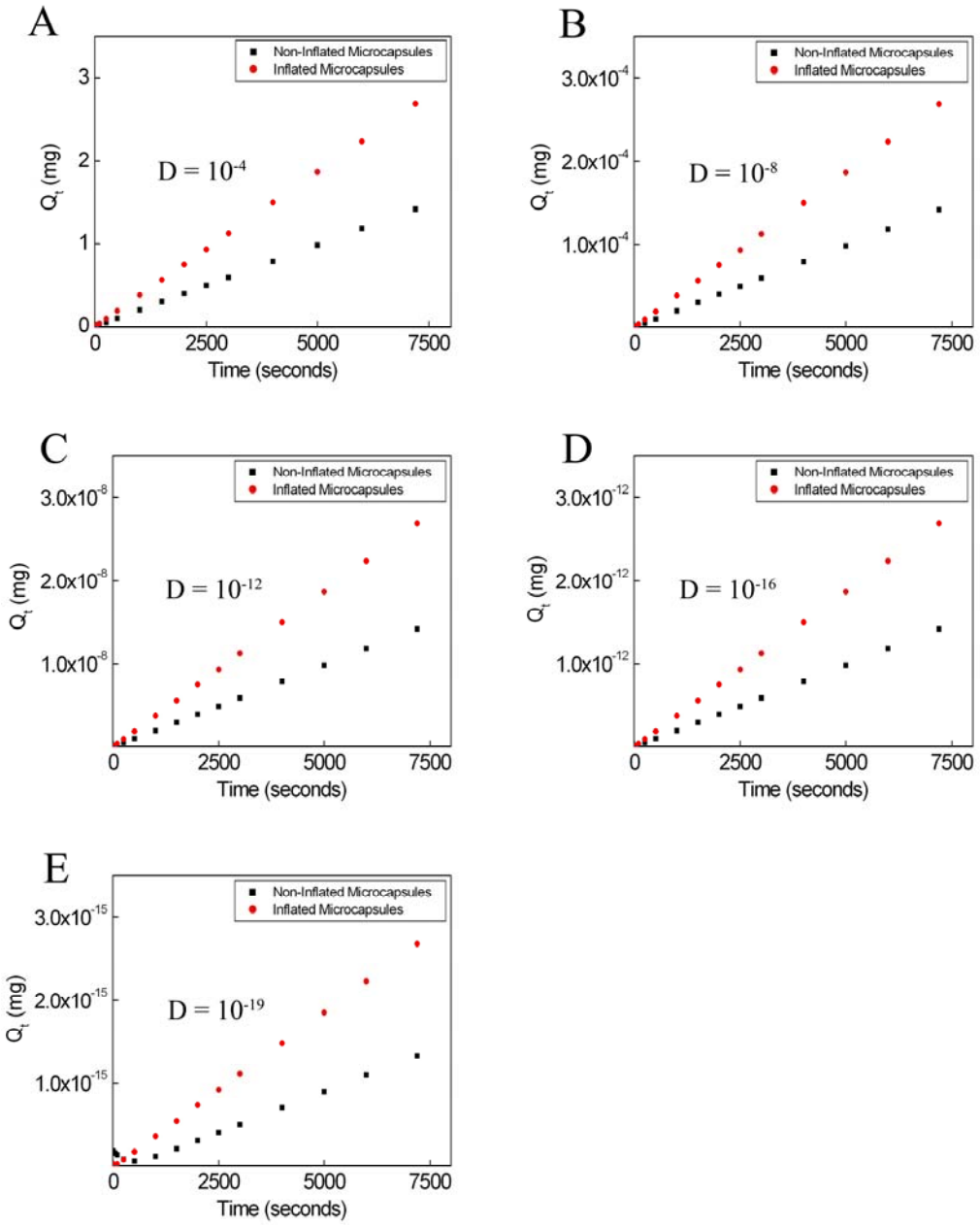

Figure S3. Total theoretical mass of dextran macromolecules, Q_t escaped from the outer surface of a non-inflated and an inflated microcapsule as a function of time, *t*. Both sets of microcapsules were considered to be fabricated with 2 bi-layers of (niPA/niPAA) and the diffusivity, *D* of dextran through the LbL capsular wall was kept constant for both microcapsules, A) 10^{-4}, B) 10^{-8}, C) 10^{-12}, D) 10^{-16} and E) 10^{-19}. The values of *D* used here are to represent the range of *D* used for the dextran of different molecular weight.

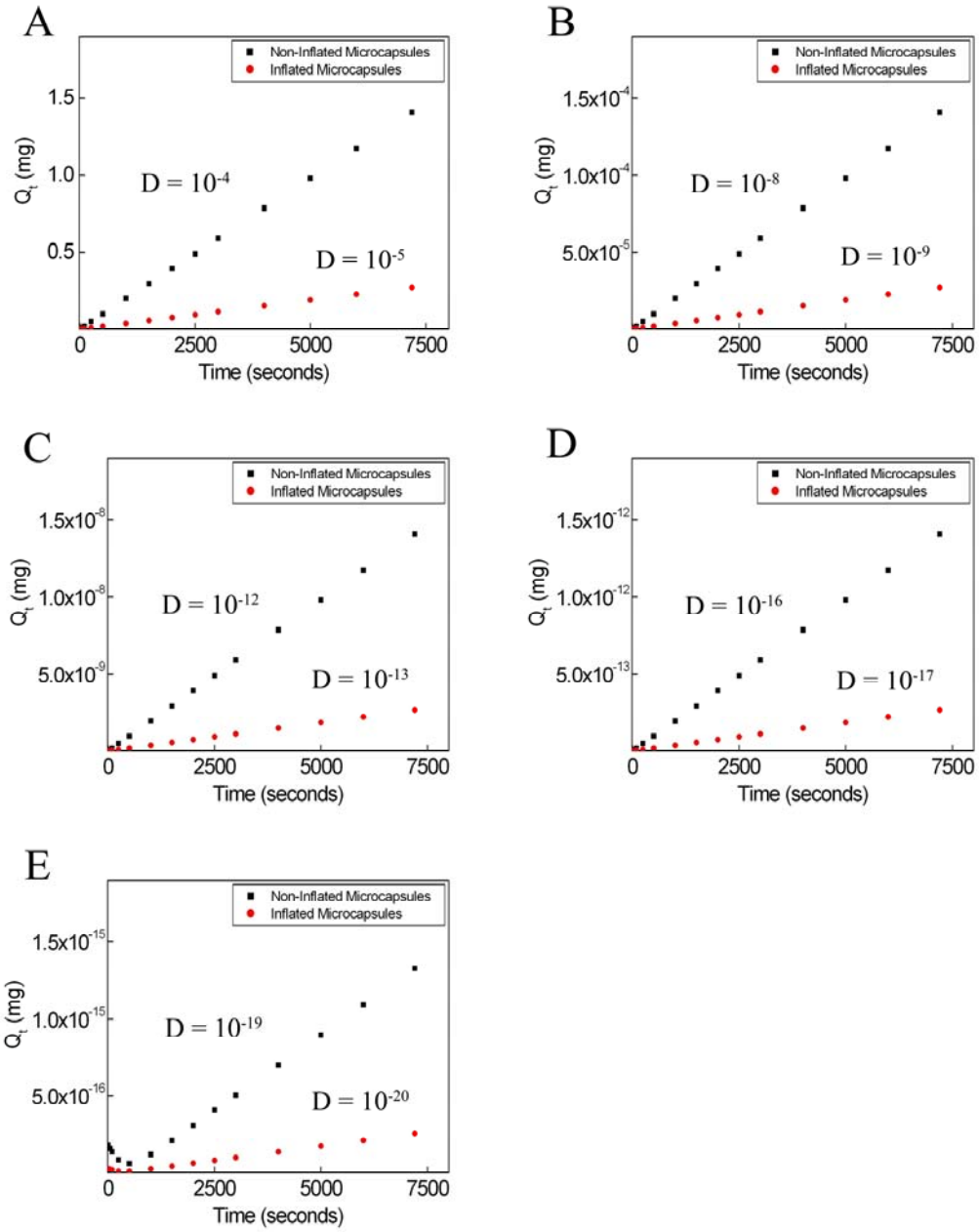

Figure S4. Total theoretical mass of dextran macromolecules, Q_t escaped from the outer surface of a non-inflated and an inflated microcapsule as a function of time, *t*. Both sets of microcapsules were considered to be fabricated with 2 bi-layers of (niPA/niPAA) and the diffusivity, *D* of dextran through the inflated LbL capsular wall was assumed to have been reduced by a factor of 10. Representative values of *D*, A) 10^{-4} & 10^{-5}, B) 10^{-8} & 10^{-9}, C) 10^{-12} & 10^{-13}, D) 10^{-16} & 10^{-17} and E) 10^{-19} & 10^{-20} are shown for the non-inflated and inflated microcapsules. The values of *D* used here are to represent the range of *D* used for the dextran of different molecular weight.