



## Characterization of Multifunctional Nanoreactors Diffusion by Pulse Field Gradient NMR

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### Introduction

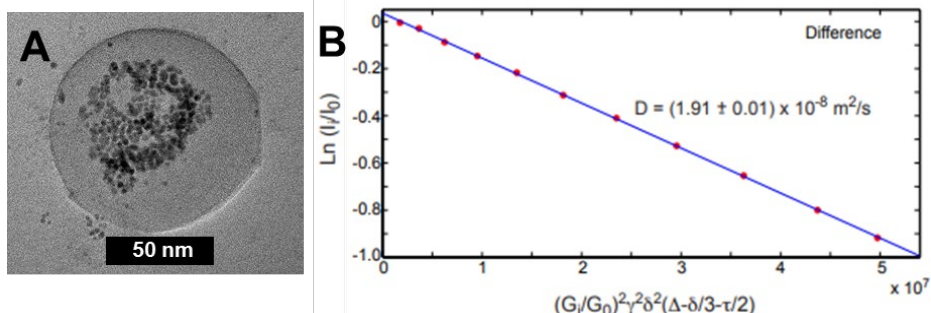
Multifunctional reactors combining reaction and separation would improve sustainability of chemical processing. Therefore, a new class of multifunctional polymer nanoreactors is being studied. The structure of the self-assembled polymer nanoreactors are analogous to oil-in-water surfactant micelles with a hydrophilic portion of an amphiphilic polymer in contact with the bulk water and hydrophobic portion (containing catalysts) sequestered in the center (**Fig. 1A**). Confining catalyzed reactions to hydrophobic polymer microenvironments accelerates reaction rates. To fully characterize the functional performance of the polymer nanoreactors, we aim to evaluate the effective partitioning of the reactant and product within the colloidal polymer nanoreactors using Pulsed-Field Gradient NMR (PFG-NMR).

### Experimental

To evaluate effective transport of reactant, 4-nitrophenol, PFG-NMR were performed using a Bruker Avance II 800 MHz NMR with a 5-mm coil  $^1\text{H-X-Y}$  TBI solution state cryo-NMR probe operating at a narrow-bore and 18.8 T magnet with 50 G/cm gradient along the z-direction. The self-diffusion coefficients  $D$  were determined from the proton spin-echo intensities measured as a function of gradient pulse strength using a standard DOSY sequence. Parameters employed in our experiments were:  $g = 46.99$  G/cm;  $\Delta = 0.1$  s;  $\delta = 1$  ms;  $\tau = 514$   $\mu\text{s}$ . A standard solution (1%  $\text{H}_2\text{O}/99\%$   $\text{D}_2\text{O}$ , doped with 0.1 mg  $\text{GdCl}_3$ ) with established diffusion coefficient ( $1.872 \times 10^{-9}$   $\text{m}^2/\text{s}$  at 298 K) was used for calibration. Saturation transfer difference (STD) spectroscopy was used to isolate the solute molecules associated with the nanoreactors. The diffusion coefficient was determined from the solute peak intensity as a function of gradient strength.

### Results and Discussion

Results of saturation transfer differentiated PFG-NMR of 4-nitrophenol in a solution of polystyrene nanoreactors. The blue line corresponds to the curve fit (**Fig. 1B**). The difference spectrum corresponds to signal from the 4-nitrophenol in closest proximity to polystyrene (within the nanoreactors) which demonstrates an effective diffusion coefficient within the nanoreactors of  $1.9 \times 10^{-8}$   $\text{m}^2/\text{s}$ . This effective diffusion coefficient was combined with observed kinetics of 4-nitrophenol reduction to perform scaling analysis to evaluate potential diffusion transfer limitations using the second Damköhler number ( $\text{Da}_{II}$ ), which is a ratio of the reaction rate to the diffusion rate. Based on an effective diffusion coefficient measured by NMR, the  $\text{Da}_{II} \sim 10^{-6}$  indicating the rate of reaction is much slower than diffusion resulting in a reaction limited system and the nanoreactor performance is dictated by the catalyst.



**Fig.1** (A) Transmission electron microscopy of nanoreactors and (B) difference spectra corresponding to the 4-nitrophenol within the nanoreactors.

### Conclusions

Saturation transfer difference (STD) spectroscopy and PFG NMR were combined to experimentally determine an effective diffusion coefficient of the reactant within the polymer nanoreactor. This measurement was combined with observed kinetics and scaling analysis to determine that the functional performance is dictated by the catalyst performance.

### Acknowledgements

The National High Magnetic Field Laboratory is supported by the National Science Foundation through NSF/DMR-1157490/1644779 and the State of Florida. In addition, this material is based upon work supported by the National Science Foundation under grant no. CMMI-1651957 (CT).

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