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# Self-Diffusion of Linear Polymers within Microcapsules

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ABSTRACT: We present a new strategy for the heterogenization of catalysts. The strategy relies on the containment of soluble polymers within a polyurea microcapsule. Diffusion ordered spectroscopy and spin−spin relaxation measurements are used to demonstrate that the encapsulated polymer is behaving as if it is in solution, not as a solid. Since the interior polymer behaves as if it is in solution, it should be possible to modify the capsule and polymeric contents separately.

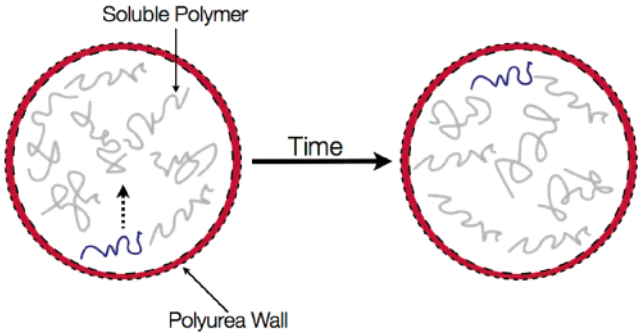
## Introduction

Our group is interested in the development and application of site-isolated catalysts for multistep, one-pot synthesis.[1,2] Heterogeneous site-isolated catalysts are ubiquitous in modern synthetic procedures. One common method for creating a heterogeneous catalyst is by covalent attachment to cross-linked polymeric resins like polystyrene (Merrifield resins) or polystyrene-*co*-poly(ethylene glycol) (JandaJel or Tenta Gel resins). Many commonly used homogeneous catalysts have been added to polymeric supports, including DMAP,[3] the MacMillan catalyst,[4] Pd cross-coupling catalysts,[5] and the Jacobsen catalyst.[6] When considering catalysts attached to polymeric supports, facile catalyst recovery and recycling make these materials attractive for complex syntheses. However, the reaction rates are typically slower for heterogeneous catalysts than their homogeneous counterparts unless the catalyst's structure is extensively optimized.[3,4]

Catalytic resins, which typically have a cross-linker concentration between 1 and 2%, are proposed to act as solution-like environments for small molecule diffusion.[7] Numerous studies have measured the relative rates of small molecule diffusion within the resins as a function of cross-linking, swelling, and backbone structure.[8−10] These reports all illustrate that as the bead swells, both solvent and solute molecules can move more freely through the resin. This body of literature supports the model that small molecules self-diffuse through a resin as they would in a solution. This information about self-diffusion is crucial for the development of highly active heterogeneous catalysts.

NMR analysis reveals that the resin's polymeric backbone and attached catalysts retain short relaxation times, large coupling constants, and broad signals associated with solids.[11] This indicates that the supported catalyst cannot move in the same way as their homogeneous counterparts. It is our hypothesis that the rate decrease associated with resins is due to the solid-like nature of the bound catalysts. As a result, we are examining an alternate heterogenization strategy that involves the confinement of a fully soluble, catalytically active polymer within a micron size polymeric capsule via interfacial polymerization (Scheme 1). By retaining a solution-like environment within the capsule, this system potentially offers both the high rate of soluble catalysts and the ease of recovery associated with heterogeneous systems. As we begin to study the capsules' catalytic activity, it is important to establish whether the encapsulated polymer is behaving as if it remains in solution rather than becoming incorporated into the wall. In this paper, we demonstrate that linear polymers confined within polyurea microcapsules remain in the solution state with a combination of NMR relaxation and self-diffusion experiments.

**Scheme 1. Model of Encapsulated Linear Polymers and Their Self-Diffusion**




NMR experiments are most often used for structural determination, but NMR spectroscopy can also be used to characterize diffusion behavior.[11] Molecules and aggregates will diffuse differently as a function of their hydrodynamic radius, allowing for the distinction of molecules with similar or overlapping chemical shifts like oligomers and polymers or surfactants and micelles.[12] This type of experiment can also differentiate small molecules in bulk solution from those that are encapsulated or moving within a gel.[13−15]

Before measuring self-diffusion, transverse (spin−spin) relaxation ($T_2$) can be measured to characterize the local motion of the molecule within a complex system. The $T_2$ is the time necessary for the loss of coherence in the *xy* plane prior to relaxation to thermal equilibrium.[11] The $T_2$ can be measured via a Carr−Purcell−Meiboom−Gill spin echo pulse sequence (CPMG) that monitors the decrease in signal, while compensating for inhomogeneity in the magnetic field.[16] In terms of experimental results, solids have extremely short $T_2$ relaxation times relative to soluble samples.[17] Matsukawa and Ando have used $T_2$ to understand the interactions between low molecular weight polymers and insoluble gels.[14,15] The authors observed

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that decreases in $T_2$ correspond to increases in gel−polymer interactions, making the soluble polymer more solidlike.

The inherent limitation of $T_2$ measurements is that they only describe local movement. $T_2$ experiments are therefore complemented by studies of bulk self-diffusion through solution. Pulsed field gradient spin echo (PFG-SE) experiments[18,19] and 2-D diffusion ordered spectroscopy (DOSY)[20] measure the rate at which a molecule, or group of molecules, self-diffuse in the sample using a series of gradient pulses. The self-diffusion rate is dependent on size of the molecules, solution viscosity, aggregation, and noncovalent interactions between the solvent and solute. Since their initial report, both PFG-SE and DOSY have been used extensively.[12] A few of the macromolecular systems that have been characterized by diffusion NMR spectroscopy include supramolecular capsules,[13,21,22] oligomers and polymers,[23−27] lamellar phases,[28−32] cross-linked polymers and gels,[9,10,14,15,33−35] and nanoparticle suspensions.[36] In this paper, we present a new application of diffusion ordered spectroscopy to study encapsulated polymers within a polyurea shell. The polymers were found to behave as if in a viscous solution.

## Experimental Methods

**General Procedures.** All reactions were carried out under an atmosphere of nitrogen. THF was dried and deoxygenated using literature procedures.[37] All other reagents were used as received, unless otherwise noted. $^1$H NMR spectra were recorded in $CDCl_3$ on Varian Mercury 300 MHz, Inova 400 MHz, and Inova 500 MHz spectrometers operating at 299.763, 399.780, and 499.920 MHz, respectively, using residual solvent as the reference. $^{31}$P NMR spectra were recorded in $CDCl_3$ on Varian Mercury 300 MHz and Inova 400 MHz spectrometers operating at 121.346 and 161.833 MHz, respectively, using 85% $H_3PO_4$ as an external reference. GPC was carried out using a Waters instrument (M515 pump, U6K injector) equipped with a Waters UV486 and Waters 2410 differential refractive index detector and four 5 $\mu$m PL Gel columns (Polymer Laboratories; 100 Å, 500 Å, 1000 Å, and Mixed C porosities) in series. The GPC columns were eluted with THF at 40 °C at 1 mL/min and were calibrated using 23 monodisperse polystyrene standards. Elemental analysis was performed by Robertson Microlit Laboratories, Inc., in Madison, NJ.

**Phosphine Polymer Preparation. Poly(styrene-*co*-4-bromostyrene) (PS−PBS).** A 500 mL round-bottom flask equipped with a stirbar was charged with polystyrene (9.67 g, 92.85 mmol, 1.0 equiv, $M_n$ = 108 000, $M_w$ = 280 000) and nitrobenzene (200 mL) and wrapped with aluminum foil. The polymer solution was cooled to 0 °C, and bromine (14.84 g, 4.76 mL, 92.85 mmol, 1.0 equiv) was added dropwise over 2 h, after which the reaction was allowed to warm to room temperature. After 48 h, the reaction was cooled to 0 °C, and ethyl vinyl ether was added dropwise until the reaction color turned to pale yellow. The resulting polymer was precipitated by adding the reaction mixture dropwise to rapidly stirring hexanes (1600 mL) and isolated by filtration. The polymer was purified through repeated precipitations by dissolution in $CH_2Cl_2$ (100 mL) and subsequent dropwise addition to rapidly stirring hexanes (1600 mL). After three precipitations, the product was isolated as an off-white material, 13.0 g (76%). $^1$H NMR (400 MHz, $CDCl_3$): 7.4−6.9 (br m, 2.5H), 6.8−6.0 (br m, 2.0H), 2.2−0.9 (br m, 3.0H). GPC (UV): $M_n$ = 105 000, $M_w$ = 240 000. Anal. Found for Br: 4.05 mmol/g.

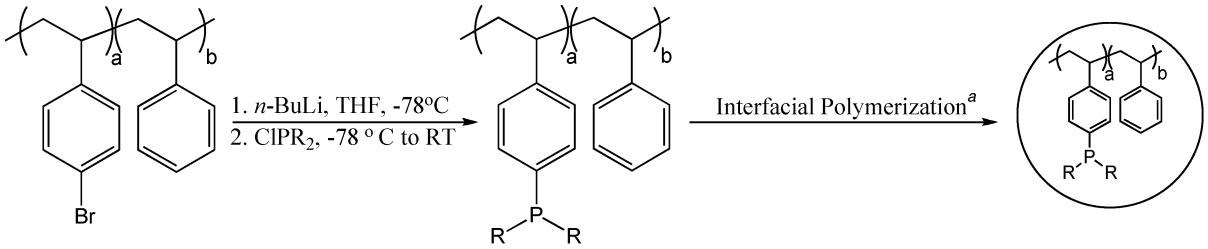
**Poly(styrene-*co*-triphenylphosphinostyrene) (TPP−PS, 1).** A flame-dried, 250 mL round-bottom flask equipped with a stirbar was fitted with an addition funnel, sealed with a rubber septum, and purged with nitrogen for 30 min. THF (75 mL) was added through the addition funnel and cooled to −78 °C. *n*-Butyllithium (12.2 mL of a 1.1 M solution in *n*-hexanes, 13.37 mmol, 1.1 equiv) was transferred to the addition funnel via syringe and added to the THF at −78 °C. A flame-dried, 200 mL round-bottom flask was charged with PS−PBS (3.00 g, 13.37 mmol, 1.0 equiv), sealed with a rubber septum, and purged with nitrogen for 30 min. THF (75 mL) was added under nitrogen, and the resulting polymer solution was transferred via cannula to the addition funnel. The polymer solution was added dropwise to the rapidly stirring *n*-butyllithium/THF solution over a period of 1 h at −78 °C. After the addition was complete, the reaction mixture was stirred at −78 °C for an additional 30 min. A flame-dried, 50 mL conical flask was charged with diphenylchlorophosphine (2.95 g, 2.40 mL, 13.37 mmol, 1.1 equiv), sealed with a rubber septum, and purged with nitrogen for 30 min. THF (25 mL) was added under nitrogen, and the resulting solution was transferred via cannula to the addition funnel. The THF solution of diphenylchlorophosphine was added dropwise to the reaction mixture over a period of 1 h. After the addition was complete, the reaction was stirred for an additional 2 h at −78 °C and warmed to room temperature for 30 min. A small amount of insoluble gel-like material was removed from the reaction mixture by filtration through a 1 in. pad of glass wool. After treating the filtrate with saturated $NH_4Cl$ (25 mL), THF was removed by rotary evaporation. $CH_2Cl_2$ (100 mL) was added, and the mixture was transferred to a separatory funnel containing saturated $NaHCO_3$ (75 mL). The organic layer was removed, and the aqueous layer was extracted with $CH_2Cl_2$ (2 × 100 mL). The combined organic extracts were washed with brine (100 mL), dried over $Na_2SO_4$, and concentrated to provide a pale yellow residue. The residue was dissolved in $CH_2Cl_2$ (75 mL) and precipitated by dropwise addition to rapidly stirring hexanes (1200 mL). The resulting precipitate was collected by filtration and dried under vacuum to provide a white solid, 3.4 g (79%). $^1$H NMR (400 MHz, $CDCl_3$): 7.8−6.0 (br m, 8.5H), 2.4−1.0 (br m, 3.0H). $^{31}$P NMR (162 MHz, $CDCl_3$): −5.48 (br s). GPC (UV): $M_n$ = 99 000, $M_w$ = 237 000. Loading (determined by $^1$H NMR): 1.9 mmol/g phosphine.

**Poly(styrene-*co*-di-*o*-tolylphenylphosphinostyrene) (OTP−PS, 2).** The procedure used to generate **1** was repeated using di-*o*-tolylchlorophosphine (in place of diphenylchlorophosphine. A white solid was isolated (65%). $^1$H NMR (500 MHz, $CDCl_3$): 7.4−5.8 (br m, 19.2H), 2.6−2.2 (br s, 6.0H), 2.2−0.9 (br m, 9.0H). $^{31}$P NMR (121 MHz, $CDCl_3$): −21.6; GPC: (UV) $M_n$ = 101 000, $M_w$ = 204 000. Loading (determined by $^1$H NMR): 1.9 mmol/g phosphine.

**Representative Encapsulation Procedure.** All compounds were deoxygenated prior to encapsulation. To a 250 mL Erlenmeyer flask was added a deoxygenated aqueous solution of poly(vinyl alcohol) (150 mL, 0.5% w/w in DI $H_2O$, $M_w$ = 89 000−98 000, 99+% hydrolyzed). The organic phase, consisting of deoxygenated $CHCl_3$ (17 mL), poly(methylene (polyphenyl) isocyanate) (3 mL, 1 equiv isocyanate, 30% incorporation), and TPP−PS (0.51 g), was dispersed in the aqueous phase using an IKA Ultra-Turrax T25 homogenizer at 6500 rpm for 2 min. The resulting emulsion was transferred to another 250 mL Erlenmeyer flask, equipped with a 1 in. stir bar, sealed with a rubber septum, and placed under an atmosphere of nitrogen. Once stirring, a second aqueous phase consisting of tetraethylenepentamine (100 $\mu$L, 0.17 equiv) in a deoxygenated solution of poly(vinyl alcohol) (20 mL) was added to the emulsion via syringe. The emulsion was allowed to stir gently overnight under positive nitrogen pressure. The resulting microcapsules were isolated by centrifugation and washed with DI $H_2O$ (2 × 200 mL), EtOH (2 × 200 mL), and $Et_2O$ (1 × 100 mL). The microcapsules were dispersed in $Et_2O$ (100 mL), transferred to a 250 mL round-bottom flask, concentrated by rotary evaporation, and dried under vacuum to yield a free-flowing powder. Characterization was performed using light microscopy (Leica DM IL). The resulting capsules were stored under inert conditions. To determine whether the polymer was remaining in the capsules, they were Soxhlet extracted with THF for 12 h. The capsules were analyzed before and after extraction by elemental analysis. The percentage of phosphorus in the sample actually increased from 0.8% to 1%, indicating that wall materials had been extracted away, but the phosphorus remained in the capsules.

**Relaxation Experiments.** $T_2$ experiments were run using a CPMG pulse sequence (CPMGT2) on an Inova 500 MHz spec-

**Scheme 2. Synthesis of Phosphine Polymers and Microcapsules**[a]




PS-PBS

**1**: R = phenyl, TPP Modified Polystyrene (TPP-PS)
**2**: R = o-tolyl, OTP Modified Polystyrene (OTP-PS)
**3**: R = phenyl, TPP-PS Cap
**4**: R = o-tolyl, OTP-PS Cap

[a] Poly(methylene (polyphenyl) isocyanate) in chloroform reacted with an aqueous phase containing poly(vinyl alcohol) and tetraethylenepentamine.

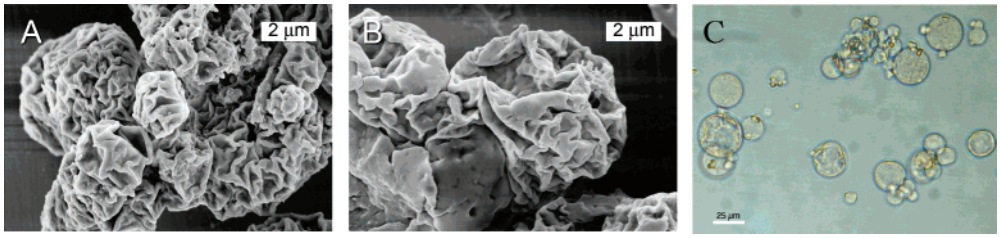



**Figure 1.** SEM images of capsules: (A) TPP−PS Cap (**3**); (B) OTP−PS Cap (**4**); (C) Swollen TPP−PS Caps (chloroform).

trometer. The delay between pulses was set to $5T_1$ to allow for complete relaxation. After running the experiment consisting of 6−8 different array values, the first spectrum in the array was phased and then all were baseline corrected. A $T_2$ macro, included in the Varian software, was used to calculate the relaxation time. Typically a sample was analyzed multiple times, first with a broad array of $T_2$ times and then with a narrower range around the approximate value.

**Self-Diffusion Experiments.** Self-diffusion was measured for each polymer and the capsules by monitoring the phosphorus nuclei at 202.36 MHz on an Inova 500 MHz spectrometer. The samples were made in $CDCl_3$ (99.8% D, 0.05% w/v TMS) purchased from Cambridge Isotope Laboratories. Specific concentrations are included for each sample in the Supporting Information. The capsules were added to the NMR tube (∼100 mg/ sample) and then swollen in 0.5 mL of $CDCl_3$. These samples were tapped to remove air bubbles, leaving a tube tightly packed with the swollen capsules. The tight packing was aided by the polydispersity of the capsule sample. Each NMR sample was run under identical PFG-SE conditions three times. The double-stimulated-echo sequence with bipolar gradient pulses (Dbppste_cc) was used for each experiment.[38] The typical experiment was run at 20 °C with 8−10 distributed steps containing between 1 and 200 transients, depending on the concentration of phosphorus in the sample. During each of these runs, the sweep width was 10 000 Hz with a transmitter offset of −5070 Hz. The gradient pulse strengths were varied from 0.002 to 0.553 T/m with bipolar pulses of 2−5 ms in total duration. The self-diffusion time was varied from 0.5 to 4 s to accommodate the range of self-diffusion rates being tested. The specific gradient ranges, times, numbers of transients, and increments are available in the Supporting Information.

**Data Analysis.** Each FID was treated with line broadening of 10 Hz for capsules and polymers and 1 Hz for small molecule samples. The spectrum resulting from the first gradient level was phased, and all spectra were baseline corrected prior to analysis. The intensity of each peak was measured by integration. The integrals were then used to calculate self-diffusion according to the method of Jerschow and Muller.[38] The natural log of the normalized integral values were then graphed against $Q$, which is a quotient of a time constant and the gradient strength squared (eq 1.) The slope of the resulting line is equivalent to the negative of the self-diffusion constant. Each sample was analyzed three times, and the resulting slopes were averaged. Data analysis was carried out using Excel and Sigma Plot 8.0.

$$\ln\left(\frac{I}{I_0}\right) = -Dg^2\gamma^2\delta^2\left(\Delta + \frac{4}{3}\delta + \frac{3}{2}\tau\right) \quad (1)$$

## Results and Discussion

To explore the dynamics of the encapsulated polymers, two types of phosphine-containing polymers were synthesized (Scheme 2). From an analytical standpoint, these polymers have the advantage of containing phosphorus nuclei that can be observed without interference from the polyurea shell. These polymers, based on triphenylphosphine grafted to polystyrene (TPP−PS, **1**) and tris(*o*-tolyl)phosphine on polystyrene (OTP−PS, **2**), are of interest as nucleophilic catalysts and as ligands for transistion metal catalysts.[39−41] The polymers were first analyzed in solution along with their small molecule analogues. The polymers were then encapsulated using an oil-in-water emulsion and interfacial polymerization creating two different encapsulated phosphines: TPP−PS Cap (**3**) and OTP−PS Cap (**4**) (Figure 1). Figure 1A,B shows the capsules in a dry state, and Figure 1C shows the capsules in full swollen. As can be seen from the images, the capsules are folded when dry but completely spherical when swollen with solvent. All NMR experiments were performed in the swollen state. The capsules were 12 wt % polymer after drying. This loading was chosen because it would provide sufficient signal for NMR analysis.

Each sample's phosphorus $T_2$ was measured using the CPMG pulse sequence on a Varian 500 MHz spectrometer (Table 1). The most noticeable changes in $T_2$ arose between the solution and solid-phase samples. When compared, the $T_2$ values for TPP−PS (**1**), TPP−PS Cap (**3**), and commercially available triphenyl phosphine on cross-linked resin (TPP−PS bead) differ by almost an order of magnitude. This substantial difference is due to the solid nature of the bead-supported phosphine. This supports the model of cross-linked polystyrene as a solvated surface. The $T_2$ values for the free OTP−PS (**2**) and OTP−PS Cap (**4**) were almost identical, indicating that the two species have similar local motions, supporting the hypothesis that the polymer remains in solution within the capsule. The capsules

**Table 1. Relaxation Times of the Phosphorus Nuclei in Phosphines and Phosphine Polymers**

| material | $T_2$ (s) |
|---|---|
| tris(*o*-tolyl)phosphine (OTP)[a] | 4.91 |
| **2** (OTP−PS) | 0.70 |
| **4** (OTP−PS Cap) | 0.65 |
| triphenylphosphine (TPP)[a] | 6.0 |
| **1** (TPP−PS) | 0.55 |
| **3** (TPP−PS Cap) | 0.18 |
| TPP polystyrene bead (TPP−PS bead) | <0.02 |

[a] The small molecule phosphines have fewer relaxation pathways relative to the polymers, leading to slower $T_2$ relaxation.

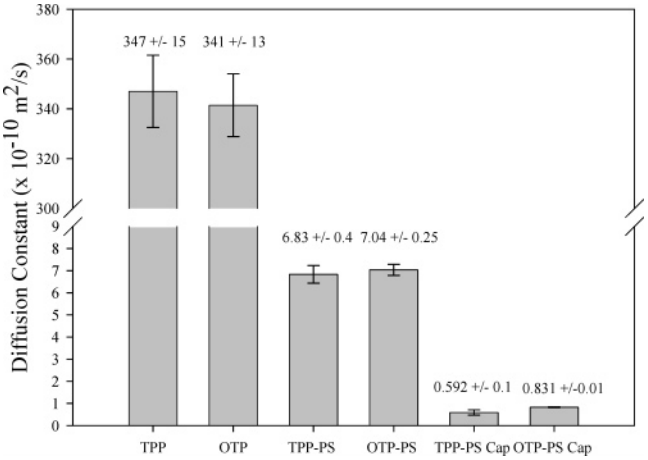



**Figure 2.** Relative self-diffusion of small molecule phosphines (triphenylphosphine (TPP) and tris(*o*-tolyl)phosphine), polymeric phosphines (**1**, **2**) at a concentration of 26 mg/mL, and encapsulated polymers (**3**, **4**.) Error is the deviation in self-diffusion rate from three or more identical self-diffusion experiments.

themselves are tightly packed into the NMR tube with enough solvent to sufficiently to swell the capsules. The movement of the capsules should be minimal relative to that of the polymers.

Given the similar local mobility of the polymer inside and outside of the capsules, the self-diffusion of each species was measured. A double-stimulated-echo experiment with bipolar gradient pulses was used to eliminate any convection effects from the self-diffusion experiment.[38] Each sample was analyzed three times, and the self-diffusion constants were averaged. The specific diffusion delays and gradient strengths were varied to accommodate the differing self-diffusion rates between samples.

To calculate the relative self-diffusion of each species, especially given the necessary changes in experimental conditions between samples, the modified Bloch−Torrey equation put forth by Jerschow and Muller (eq 1) was used.[38] In this equation, $I/I_0$ is the normalized signal intensity, as measured by integration at each gradient step. $I_0$, in this case, is the integral value at the weakest gradient strength. The value of $g$ is the gradient strength in T/m, and $\gamma$ is the magenetogyric ratio in $T^{-1}$ $s^{-1}$. The other three variables are constant through a single experiment: $\delta$ is the gradient length, $\Delta$ is the self-diffusion delay, and $\tau$ is the gradient recovery time.

After measuring the self-diffusion constants for each substance, we found that small molecule phosphines self-diffused significantly faster than even dilute polymer samples (Figure 2). Self-diffusion is a function of both viscosity and hydrodynamic radius, explaining why the increase in molecular weight and viscosity caused the polymer to self-diffuse more slowly. As seen in Figure 2, the encapsulated polymers self-diffuse significantly (10×) more slowly than their soluble counterpart. We hypothesize that a high viscosity inside the capsule causes the slow rate of self-diffusion. To test the effect of polymer concentration on self-diffusion rate, a series of soluble OTP−PS (**2**) samples were compared.

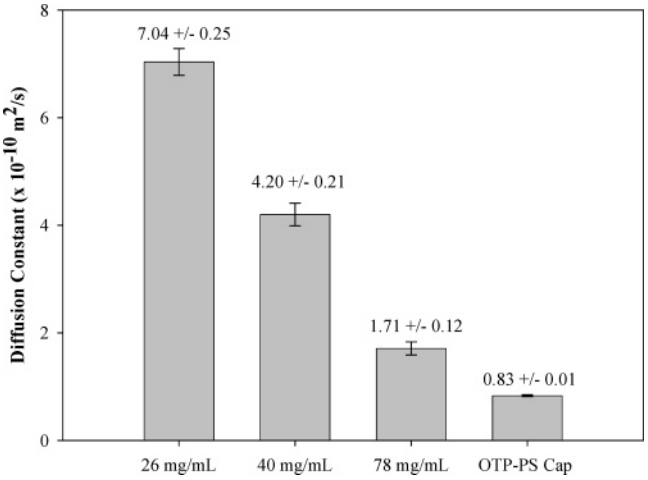



**Figure 3.** Comparison of self-diffusion behavior of OTP−PS (**2**) at various concentrations with its self-diffusion within the capsule.

As anticipated, we found that as the concentration of OTP−PS (**2**) increased from 26 to 78 mg/mL, the self-diffusion rate decreased from $7 \times 10^{-10}$ to $1.71 \times 10^{-10}$ $m^2/s$ (Figure 3). The same trend is observed as the concentration of TPP−PS (**1**) is increased (Supporting Information). The rate of self-diffusion at the highest measured OTP−PS concentration approaches that of the polymer's self-diffusion within the capsule ($0.83 \times 10^{-10}$ $m^2/s$, OTP−PS Cap). This observation supports the hypothesis that self-diffusion is limited by a high local polymer concentration within the capsule.

To estimate an interior concentration for the capsules, the three self-diffusion constants measured for OTP−PS were fit to a curve,[42] which were then used to estimate the concentration at a self-diffusion constant of $0.83 \times 10^{-10}$ $m^2/s$. The interior concentration should be ∼84 mg/mL for OTP−PS Cap. The minimum concentration of polymer within the capsules would be 26 mg/mL if the walls were infinitely thin, as determined by the concentration of polymer in the emulsion disperse phase before encapsulation. The capsule walls, however, should have significant volume of their own. If the wall thickness is only 3 $\mu$m, the interior radius of the capsule would decrease from an average of 10 $\mu$m to 7 $\mu$m, causing the concentration to approach 80 mg/mL.

To further support the hypothesis that the capsules have a high internal concentration and viscosity, the self-diffusion of methylene chloride was measured and compared in d-chloroform, a 33 mg/mL TPP−PS (**1**) solution, and a sample of TPP−PS Cap (**3**). The rate of methylene chloride self-diffusion dropped by more than 60% in the capsule sample relative to free solution (see Supporting Information). The slowing of small molecule self-diffusion offers evidence that that the capsule sample, as a result of both interior polymer concentration and swollen wall matrix, is a viscous environment. An alternative view of the slower self-diffusion rate of the encapsulated polymer is either that the walls confine the polymers within a volume that is smaller than the mean free path or that the shell walls can bind with the polymer, preventing rapid self-diffusion. On the basis of the presented data, both hypotheses might be valid.

## Conclusions

The encapsulated polymers are behaving as if in a viscous solution, with both $T_2$ relaxation times consistent with solution

phase polymers and observable self-diffusion. The demonstration of the solution-phase behavior provides support for the model of polymeric microcapsules as a solid shell surrounding a solvent filled core. Since the core and shell act as two separate environments, it should be possible to tune each individually. This provides flexibility to modify both core components, like catalyst loading and polymer structure, as well as the wall components, which alter swelling properties, self-diffusion rates, capsule size, and strength. This flexibility should speed optimization as we begin to examine the catalytic promise of microencapsulated linear polymers.

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**Supporting Information Available:** Specific NMR parameters for each self-diffusion experiment, raw self-diffusion data, and relaxation data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(42) The three points (concentration, diffusion) with a three-parameter power function, $y = mx^b + c$, and an exponentail decay curve, $y = me^{bx} + c$. Both curves gave values approximately 84 mg/mL for predicted interior concentration.

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