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Microencapsulated Linear Polymers: "Soluble" Heterogeneous Catalysts

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Catalysts are often the most expensive component of a reaction and are frequently difficult to separate from the product. A wide variety of solid supports are used to facilitate catalyst removal and recycling.[1−8] Cross-linked polymers are especially flexible supports for organo-catalysts and ligands because myriad methods are available for covalent attachment.[7,9−14] The high surface area and porous structure allow small molecules to rapidly diffuse in and out of the polymeric supports.[15,16] The catalysts on the support, conversely, diffuse very little and experience a different solvation environment than homogeneous catalysts, often rendering them less selective and less active, unless painstakingly optimized.[9,10]

It would be desirable to have a system that combines the ease of cross-linked polymers with the catalytic activity of homogeneous catalysts. Inspired by recent work of Ley[7] and others,[17,18] we propose that catalysts attached to soluble polymers entrapped within microcapsules will yield higher activities and be more readily tunable than catalysts attached to cross-linked resins.[19] In this paper, we provide the first example of catalysis using encapsulated linear polymer−catalyst conjugates. This new approach not only provides a more active catalyst than that supported on cross-linked-polystyrene but also allows for simpler tuning.

The model reaction we investigated is a 4-(*N*,*N*-dimethylamino)-pyridine (DMAP)-catalyzed acylation. DMAP is an ideal model because it has been studied as a small molecule,[20,21] on linear polymers,[22−24] inorganic supports,[25−27] and insoluble polymeric supports.[9,28−33] DMAP is also extremely sensitive to its electronic environment, as demonstrated by the extensive linker and backbone changes required to optimize its activity on polymeric support.[9,28,34] In contrast, we show that catalytic microencapsulated polymers can be optimized with minimal synthetic modification.

The microencapsulated polymer is synthesized in two steps.[19] The DMAP-modified linear polystyrene (LPSDMAP, **2**) is formed by a copolymerization of a DMAP-modified monomer (**1**) and styrene (Scheme 1). LPSDMAP is then dissolved in chloroform along with poly(methylene[polyphenyl]isocyanate) (PMPPI). This organic phase is then dispersed in an aqueous phase containing poly(vinyl alcohol) as a stabilizer. The interfacial polymerization is initiated with tetraethylenepentamine (TEPA). Once washed and dried, the capsules are isolated as a free-flowing solid (Figure 1).

Acylation of *sec*-phenethyl alcohol with acetic anhydride in tetrahydrofuran (THF) was used as the test reaction. The capsules were compared to a commercially available (dimethylamino)-pyridine on polystyrene-*co*-divinylbenzene (PSDMAP), as well as LPSDMAP (**2**), and the small molecule model, 4-(*N*-benzyl-*N*-methyl)aminopyridine (BMAP) (Table 1). As shown in Table 1, the rate of acylation is cut in half between DMAP and its benzyl derivatives (BMAP and LPSDMAP). BMAP's rate is then decreased by another factor of 4 when attached to an insoluble support (PSDMAP). The initial microcapsule samples gave rates similar to those for PSDMAP (Table 1). The encapsulated catalyst is simply filtered off after the reaction is complete and is reusable. In three rounds of recycling, we see little change in rate or reaction yield (99, 97, and 94%).

The exciting feature of microcapsules is that a number of factors can be changed to create capsules with a desired strength, permeability, or size, without changing the interior polymer.[35] In

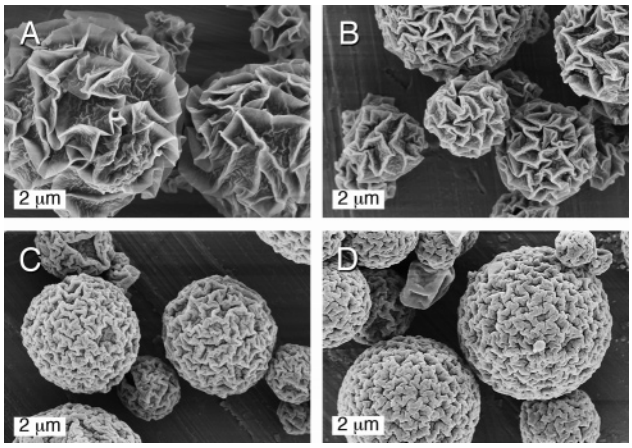


Figure 1. SEM images of microcapsules containing LPSDMAP. A−D are made with 5, 7, 13, and 17% PMPPI, respectively. SEM images and size distribution data are available in Supporting Information.

Scheme 1. Synthesis of DMAP Polymer and Microcapsules

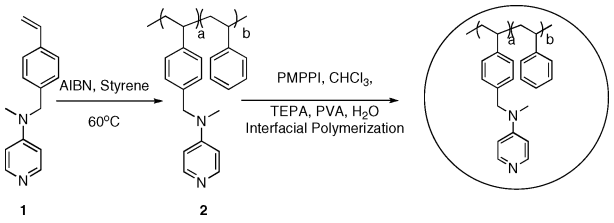
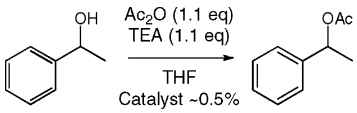


Table 1. Relative Rates of Acylation of *sec*-Phenethyl Alcohol in the Presence of 0.5 mol % of Catalyst



catalyst	k_{rel}[d]	conversion
DMAP	9.2	99%
BMAP	4.2	98%
LPSDMAP (**2**)	5.1	98%
PSDMAP	1.0	89%
unoptimized LPSDMAP capsule[a]	0.9	
LPSDMAP capsule[b]	3.2	91%
LPSDMAP capsule[c]	2.8	84%[e]

[a] PMPPI (7%), THF wash. [b] PMPPI (5%), no THF wash. [c] PMPPI (5%), THF wash. [d] Background $k_{rel} = 0.007$. The reaction rates were measured using the method of initial rates. [e] The THF washing may expose amines in the shell that partially hydrolyze the acetic anhydride.

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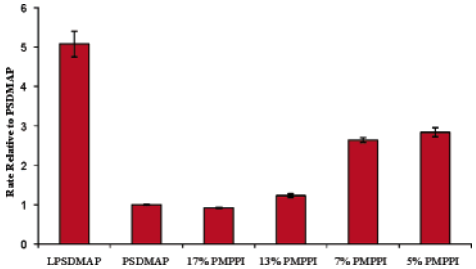
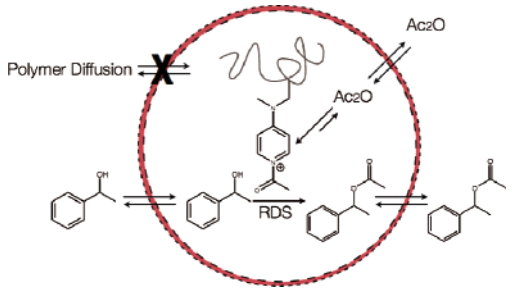


Figure 2. Comparison of rates of LPSDMAP (**2**) and PSDMAP (Fluka, 3 mmol/g) to THF-washed capsules made with varied PMPPI loading (5−17%).

Scheme 2. Model of DMAP Capsule Catalysis



this case, we achieved the optimized rate (Table 1) of the encapsulated DMAP catalyst by varying the wall thickness of the microcapsules. Wall composition was varied by changing PMPPI concentration in the emulsion (Figure 1). As the amount of PMPPI is increased, the walls grow thicker, which causes the walls to collapse differently. Walls that are thin crumple like paper (Figure 1A,B), while thicker walls fold less when dried (Figure 1C,D). *By varying only the encapsulation procedure, a more active catalyst is created.* As seen in Figure 2, the catalytic activity of the capsules increases with decreasing PMPPI concentration. The final catalyst was approximately 3-fold faster than PSDMAP.

Recovered capsules were examined by both light and electron microscopy after each reaction to establish that the capsule walls did not rupture under reaction conditions. Since capsule rupture was not evident, the possibility of polymer diffusion through the wall had to be considered. To test whether the catalyst was leaching from the capsules, we extracted them with THF using a Soxhlet apparatus. No significant decrease in catalytic activity was observed.[36] Since THF is an excellent solvent for the entrapped polymer, these data indicate that the linear polymers are too large to diffuse through the capsule shell (Scheme 2).

Since the polymer remains within the capsule throughout the reaction and the PMPPI concentration affects the rate of catalysis, we conclude that reagents, substrates, and products must enter and exit the shell faster than the acylation occurs (Scheme 2). Therefore, the rate of the reaction will depend on the rate of the diffusion preequilibria as well as the rate of the DMAP acylation step. This preequilibria, we believe, is responsible for making the thin shelled capsules slower than the LPSDMAP. As the shell becomes thicker, the diffusion of molecules to the interior slows, causing the overall reaction rate to decrease (Figure 2). These data show that the shell can be used to tune the encapsulated catalyst.

In conclusion, we demonstrated that catalytic polymers can be encapsulated within microcapsules and that the polymers are retained within the capsules throughout a reaction. We also showed that by varying shell thickness the reaction rate is tuned and that with thin, strong walls the capsules' reaction rate nears that of an unencapsulated polymer. High reactivity is important because increased catalyst loadings fill the reaction vessel with resin, limiting reagent diffusion and mixing. This approach represents a new strategy for creating heterogeneous catalysts.

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Supporting Information Available: Experimental methods, DMAP loading determinations, rate data, capsule size data, and SEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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