

# Liquid/liquid separation of polysiloxane-supported catalysts†

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**Liquid/liquid separation after monophasic reactions is a viable way to use and recover polysiloxane-supported catalysts.**

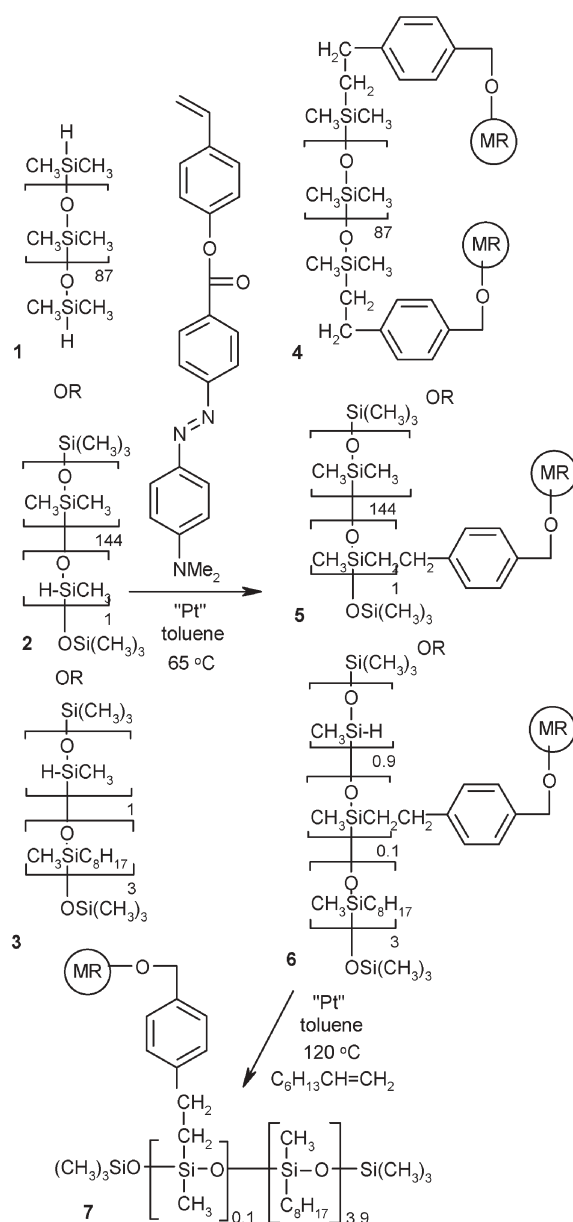
Polymer supports used in synthesis most commonly are based on organic materials and typically are recovered by filtration after a reaction. Insoluble inorganic materials in the form of inorganic metal oxides (e.g. functionalized silica gel) or meso-porous supports (e.g. zeolites) are also widely used. Soluble inorganic polymers like polysiloxanes or polyphosphazenes are well-known, common materials<sup>1</sup> but have received limited attention as supports for catalysts.<sup>2–6</sup> A recent report also described a polysiloxane-supported organic catalyst.<sup>7</sup> In all of these cases, precipitation or a membrane separation is used to recover/re-use the supported catalyst. Our success in developing liquid–liquid based separations of soluble organic polymer-bound catalysts from products after a homogeneous reaction<sup>8,9</sup> and the excellent tunable solubility of polysiloxanes suggested to us that inorganic polymers have potential as soluble supports that could be separable from products using liquid/liquid biphasic separations. This work shows that commercially available polysiloxanes can be easily modified and used to address the strategic issue of catalyst separation.<sup>10</sup>

The work reported herein uses polysiloxanes as soluble inorganic polymer supports for an organocatalyst. Linear polysiloxanes (Si–O–Si) are widely used as fluids, surfactants, release agents, and lubricants.<sup>11</sup> These materials are low polarity, hydrophobic polymers with very low glass transition temperatures and are often available as viscous oils or gums soluble in many organic solvents. Polysiloxanes possess good thermal, oxidative, chemical, and biological stability and are commercially available with silane (Si–H) functionality. Thus, it is surprising that they have been relatively little used as catalyst supports.<sup>3–7</sup>

While polysiloxane-bound catalysts are known, separations of these catalysts have generally not focused on using solubility as a separation tool. To explore the potential of using polysiloxane phase selective solubility in separation, we prepared several polysiloxanes containing an azo dye. The azo dye served as a surrogate for a catalyst and facilitated analysis of the phase separability of these soluble polymers.<sup>12,13</sup> As shown in Scheme 1, a collection of three different commercially available dimethyl polysiloxanes containing terminal or pendant silanes (1–3) were hydrosilylated with a vinyl-containing azo dye. In one instance, a

limited amount of the dye was used and a simple alkene was used to convert the remaining Si–H into Si–octyl groups. This produced a collection of four dye-labeled polysiloxanes 4–7 whose phase selective solubility was subsequently tested.

To test the feasibility of liquid/liquid biphasic separation for recovery of 4–7, the dye-labeled polysiloxane was dissolved in a



**Scheme 1** Synthesis of dye-labeled polysiloxanes 4–7.

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**Table 1** Phase selective solubility for polysiloxanes (**4–7**) in biphasic mixtures formed thermomorphically or by water addition

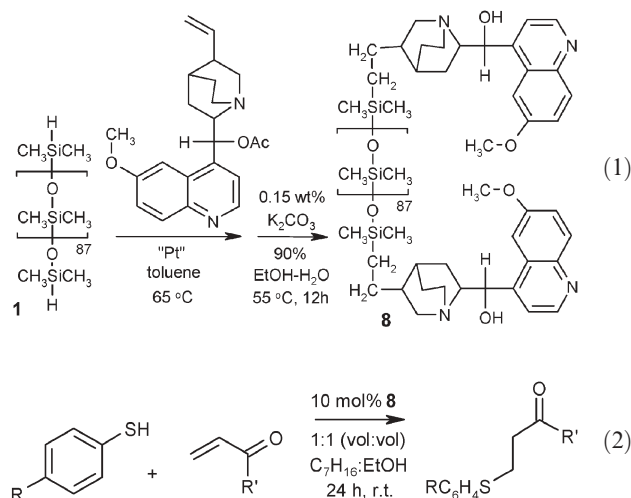
Polymer	Solvent mixture	Phase selective solubility <sup>a</sup> (% dye in heptane-rich phase)
<b>4</b>	heptane/DMF	97.6
<b>5</b>	heptane/DMF	99.7
<b>6</b>	heptane/DMF	94.2
<b>7</b>	heptane/DMF	98.8
<b>4</b>	heptane/aq. EtOH	99.6
<b>5</b>	heptane/aq. EtOH	99.5
<b>6</b>	heptane/aq. EtOH	99.5
<b>7</b>	heptane/aq. EtOH	99.3

<sup>a</sup> Phase selective solubilities were measured after 2 phase separation cycles. Further phase separation cycles led to modest improvements in phase selectivity (e.g. **6** in heptane/DMF had 97.7% phase selective solubility after 6 phase separation cycles).

thermomorphic mixture of heptane and DMF or heptane and EtOH. The first solvent mixture is a thermomorphic solvent mixture that is biphasic at room temperature and monophasic at elevated temperature. To test separations, a heptane solution of the dye-labeled polymer was mixed with an equal volume of DMF, heated to 70 °C, and cooled to 25 °C. The second solvent mixture is a latent biphasic mixture. The dye-labeled polymer is soluble in an equivolume mixture of heptane and EtOH but can be recovered on addition of <20 vol% water because the water addition produces a biphasic mixture with a less dense heptane phase. In all cases, the initially formed polymers **4–7** were subjected to several phase separation cycles. The first few cycles presumably removed any unreacted methyl red (or oligosiloxanes). An analysis of the heptane and the polar phases by UV-vis spectroscopy for the azo dye-labeled polysiloxane during the third phase separation served as our criteria for phase selective solubility. The results of these studies are listed in Table 1 below and show that all these polymers were phase selectively soluble in heptane. All of these polymers have phase selective solubility that is adequate for catalyst recovery/reuse in the heptane/EtOH–H<sub>2</sub>O system and **5** and **7** had almost as good phase selective solubility in heptane/DMF.

While dye-labeled polymers used as surrogates for polymer-bound catalysts simplify testing of liquid/liquid separation strategies for catalyst recovery,<sup>12,13</sup> real catalytic reactions have to be studied to show that catalyst recovery/re-use is feasible. To do this, we immobilized quinine, a cinchona alkaloid, on the siloxane support (eqn. 1). Cinchona alkaloids have vinyl groups

for immobilization and have been shown to catalyze the Michael addition of thiols to  $\alpha,\beta$ -unsaturated ketones both as monomers and as polymer-supported species.<sup>14–16</sup> Catalyst **8** (quinine attached to  $\alpha,\omega$ -bis (hydrosilyl)polydimethylsiloxane **1**) is equally effective as a recyclable Michael addition catalyst for thiol additions to  $\alpha,\beta$ -unsaturated ketones and esters (eqn. 2). As shown in Table 2, using a latent biphasic liquid/liquid separation to recover the polymeric catalyst was effective in recovery/re-use of this catalyst through 5 cycles in several examples of this reaction. As has been noted previously, the isolated yield of thioether product increased through the first few cycles in some cases. This reflects the fact that some thioether product was lost to the heptane-rich phase in the first few cycles. This effect is absent once the heptane-rich phase is saturated with the low molecular weight product.



The goal of this study was to show that liquid/liquid separations are a viable way to recover/re-use polysiloxane-bound catalysts after a monophasic reaction. In this case, quinine was a convenient vinyl-containing starting material. However, quinine is a chiral catalyst too and in one case the product thioether, 3-thiophenylcyclohexanone, is chiral. While we did not expect to see high levels of asymmetric induction in this case, we did examine the product's e.e. It was modest (20%) as expected.

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**Table 2** Product yields for Michael addition reactions catalyzed by **8** in latent biphasic mixtures over 5 cycles

Michael donor	Michael acceptor	Product yield (cycle) <sup>a</sup>
C <sub>6</sub> H <sub>5</sub> SH	H <sub>2</sub> C=CHCOCH <sub>3</sub>	83 (1); 92 (2); 100 (3); 100 (4); 100 (5)
C <sub>6</sub> H <sub>5</sub> SH	2-cyclohexen-1-one	81 (1); 100 (2); 100 (3); 97 (4); 98 (5)
C <sub>6</sub> H <sub>5</sub> SH	H <sub>2</sub> C=CHCO <sub>2</sub> Et	44 (1) <sup>b</sup> ; 82 (2); 70 (3); 86 (4); 95 (5)
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> SH	H <sub>2</sub> C=CHCO <sub>2</sub> Et	45 (1) <sup>c</sup> ; 66 (2); 55 (3); 42 (4); 42 (5)
<i>p</i> -HO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> SH	H <sub>2</sub> C=CHCOCH <sub>3</sub>	88 (1); 86 (2); 94 (3); 90 (4); 85 (5)

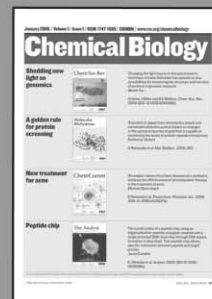
<sup>a</sup> Reactions were carried out at room temperature in 50 : 50 mixtures of heptane and EtOH using 10 mol% **8** as catalyst. After the reactions were complete (GC assay), addition of 10 vol% H<sub>2</sub>O perturbed this system to form a biphasic mixture. The yields are for pure products characterized by <sup>1</sup>H NMR spectroscopy that were isolated from the aq. EtOH phase after removal of the EtOH and water at reduced pressure. Some loss of the more volatile products may have occurred during these workups. <sup>b</sup> The yield of Michael addition product using quinine (1 mol%) not immobilized on **1** was 57%. <sup>c</sup> The yield of Michael addition product using quinine (1 mol%) not immobilized on **1** was 58%.

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