arises as a result of an acceleration in the oxidative part of the process. The decreasing activity at larger alcohol concentrations may originate from the concomitant decrease in the water concentration. Consequently, the reductive reaction step may become too slow to efficiently compete with recombination of the charge carriers. The ammonia produced is further photooxidized to nitrate through traces of oxygen present in the system.

Aqueous solutions of sodium formate and humic acids of proper concentration also function as reducing agents. Since the latter compounds are ubiquitous in nature and $Fe_2Ti_2O_7$ phases could be formed through oxidative weathering of ilmenite in sunlight, this novel reaction may be an example of a light-driven nonenzymatic nitrogen fixation under natural conditions.[23]

Experimental Section

After fast immersing a glass slide (26 × 76 mm) into an ethanolic solution of $Ti(O\textit{i}Pr)_4$ and $FeCl_3$ (Fe:Ti = 1:1 or 2:1) it was pulled out at a speed of 6 cm min^{-1} and left in air for 15 min. The film was subsequently tempered for 20 min at 600 °C. Irradiations were performed on an optical train equipped with a high-pressure Hg lamp (HBO 200) mounted at a distance of 35 cm from the solidex glass cuvette ($\lambda \geq 320$ nm, 80 × 40 × 10 mm) which contained the glass slide. Unless otherwise noted, a film with a Fe:Ti ratio of 1:1 was employed and unpurified dinitrogen was permanently bubbled through the suspension. The concentration of NH_4^+ ions was determined colorimetrically according to the method of Kruse and Mellon;[24] the resulting absorbancies at 450 nm were in the range of 0.01 to 2.10. Blank experiments in the absence of the glass slide did not induce the formation of significant amounts of ammonia. The reproducibility of the film preparation was excellent as evident by the ammonia concentrations agreeing within ± 10 %. Nitrite and nitrate were measured by ion chromatography (Dionex-120, Ion Pac AS 14 column, conductivity detector, $NaHCO_3$:Na_2CO_3 = 0.001:0.0035 mol L^{-1} as eluting agent).

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PASSflow Syntheses Using Functionalized Monolithic Polymer/Glass Composites in Flow-Through Microreactors[**]

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After an "incubation time" of more than 25 years interest in polymer-supported reagents for the solid-supported synthesis in solution has increased dramatically of late.[1] In this technique reagents or catalysts are immobilized on a solid

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[**] Part of these studies were supported by the Fonds der Chemischen Industrie and the European Community (EC project number HPRI-CT-1999-00085) for which we are grateful. PASSflow = *P*olymer *A*ssisted *S*olution-*P*hase *S*ynthesis technique in flow-through mode.

support, in many cases, crosslinked polystyrenes have been used for this purpose. The intrinsic advantages of this hybrid solid-phase/solution-phase technique lie in the simple purification and the possibility to use these reagents in excess to drive reactions in solution to completion. The opportunity to employ this technique in conjunction with continuous-flow processes is particularly appealing as this application would create an ideal almost workup-free technique for automated solution-phase synthesis.[2]

However, there are two key criteria to be considered when constructing a stoichiometrically working flow-through reactor. These are high loading and good accessibility of the soluble reactant to the active immobilized species. Both criteria can be controlled by the right choice of the solid support. For polymeric supports the degree of cross-linking is essential.[3, 4] For kinetic reasons a low degree of cross-linking is desired. This feature leads to gels, which as a result of swelling in organic solvents such as THF or dichloromethane which makes the immobilized species more accessible. However, filled in tubes these polymers either block the flow (and cause a pressure drop) when swollen or, when shrunk, create a gap between the inner wall of the flow-through reactor and the polymer allowing the solution to bypass the polymer.

Herein we present the PASSflow (*P*olymer *A*ssisted *S*olution-*P*hase *S*ynthesis flow-through mode) technique, which allows solid-phase supported synthesis in solution to be performed in a flow-through mode. This concept is based on a monolithic flow-through microreactor, which is loaded with polymer-bound reagents or catalysts and allows organic transformations in solution to be performed with a low to moderate pressure drop. Essentially, the monolithic block contains a novel, chemically functionalized, highly porous polymer/glass composite. Polyvinylchlorobenzene (cross-linked with 2–20% of divinylbenzene) is prepared by precipitation polymerization in the pore volume of highly porous glass rods to yield a polymeric matrix inside the rod (Figure 1).[5, 6] The polymeric structures obtained are small beads (1–5 μm diameter), and are all cross-linked with polymeric bridges. This property results in a monolithic polymeric phase, with a high surface area, which is wedged inside the microchannel pore system of the support. Even under forced convectional flow the polymer phase can not be washed out of the reactor. Furthermore, having a polymeric phase inside the fixed matrix of glass rods leads to reactor interiors with a stable shape. The polymer particles inside the pore volume can swell and shrink only in the pore volume, whereas the outer dimensions of the rod stay stable. Technical problems like bypassing or high pressure drop as observed in pure polymer packings can be avoided.

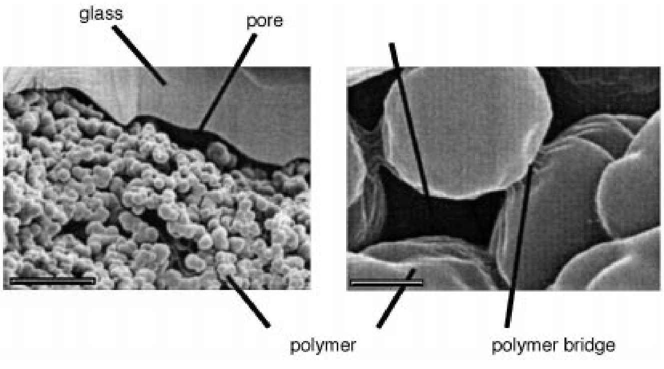


Figure 1. Scanning electron microscope image of the polystyrene/glass composite. The scale bars correspond to 10 μm (left) and 500 nm (right).

These chemically functionalized rods were first embedded inside a solvent-resistant tube. This was followed by encapsulation with a pressure-resistant fiber reinforced epoxy resin housing with two standard high-pressure liquid chromatography (HPLC) fittings (Figure 2). A particular difficulty associated with monolithic flow-through reactor systems is the suppression of the fluid bypass and forcing the fluid to flow through the microchannels of the rod. Dynamic NMR spectroscopy microscopic visualization with water as a fluid clearly showed that no solvent bypass is detected for this flow-through reactor for a pressure up to 20 bar.[7] In the example reported here, the benzylic chlorine function was aminated with triethylamine in toluene to yield the corresponding polymer-anchored quaternary ammonium ion. The resulting strongly basic ion-exchange resin was loaded with various anions. The synthetic properties of these chemically functionalized flow-through reactors were tested with fundamental transformations such as substitution, oxidation, and reduction (Table 1).

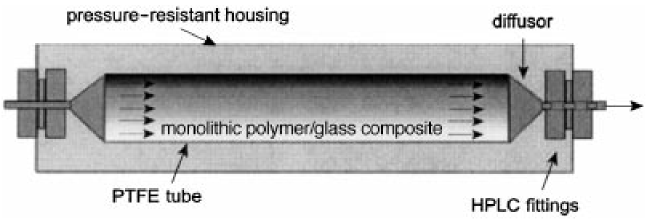
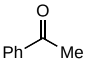
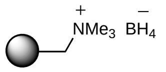
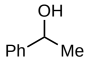
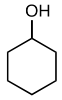
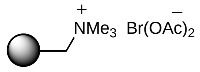
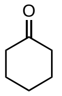
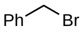
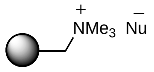
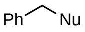
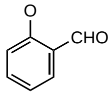


Figure 2. Schematic set up of the PASSflow reactor; PTFE = polytetrafluoroethylene.

The monolithic reactors (about 10 cm in length, about 5 mm diameter, about 10 to 20 mass% (ca. 1 mmol) polymer loading) enable the preparation of up to 1 mmol of product in shorter times than reactions promoted with conventional polymer-bound reagents. This is demonstrated for the reduction of actophenone to 1-phenylethanol using polymer-bound borohydride (Figure 3). As expected, the reaction rate is much faster when the solvent is forced to flow through the microchannels of the monolithic reactor than when a bare polymer/glass composite rod is placed in a beaker of reactant solution or with a finely powdered borohydride-impregnated composite material.[8] This result clearly demonstrates that the combination of a highly porous chemically inert glass rod and a functionalized polymer anchored inside the pores guarantees a short diffusion path for the soluble organic reactants and products and in addition enables a good convectional flow.[9]

To test the utility of our microreactors for the derivatization of natural products or drugs, we employed three differently functionalized PASSflow reactors, modified with the oxidizing anion **2**,[10] the fluoride anion **4**, and the reducing anion **6**. In a three-step sequence the partially *O*-silylated steroid **1** was transformed into the aminoderivative **7** (Scheme 1). Only

Table 1. Reactions performed with the PASSflow reactor.

Starting material	Chemical functionalization in the reactor		Conditions	Product
			MeOH, 60 °C, 6 h	
	 cat TEMPO		CH_2Cl_2, RT, 6 h	
		Nu = N_3	C_6H_6, 70 °C, 12 h	
		Nu = CN	C_6H_6, 70 °C, 12 h	
		Nu = SCN	C_6H_6, 70 °C, 12 h	
		Nu = 	Toluol, 75 °C, 24 h	

[a] The products were isolated after removal of the solvent. In each case the yield was > 95 %; according the NMR spectra the purity was > 95 % for all cases.

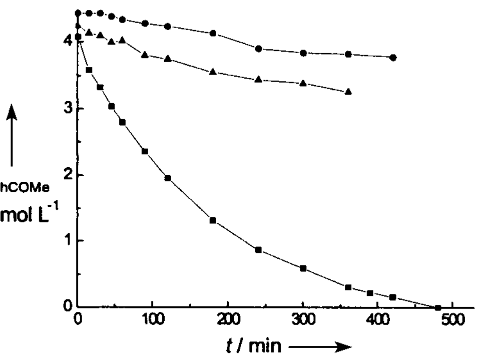
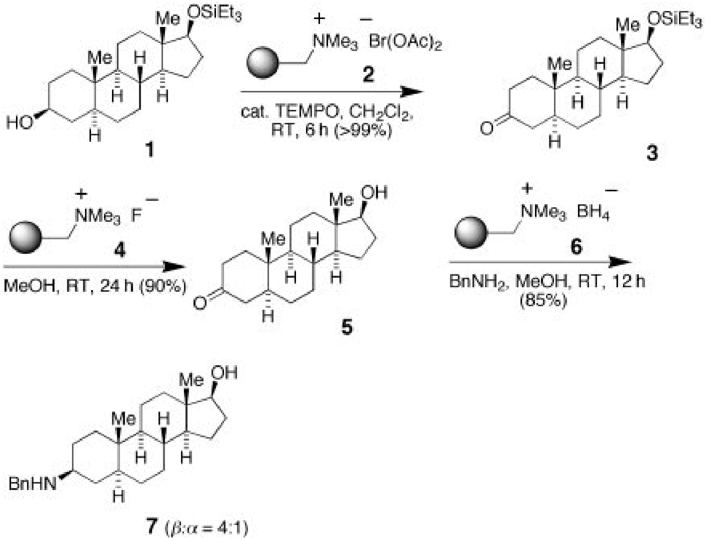


Figure 3. Borohydride-promoted reduction of acetophenone: reaction course using different composites (■ microreactor, ● bare chunks of monolithic glass rod, ▲ powdered composite).



Scheme 1. Polymer-assisted three-step derivatization of a steroid in PASSflow reactors; TEMPO = 2,2,6,6-tetramethylpiperidine *N*-oxide OAc = acetate.

anions were immobilized which ensures the simple regeneration of the reactor column after each reaction.[11] The TEMPO-catalyzed oxidation of alcohol **1** with the polymer-bound bromate(I) anion **2** gave ketone **3**, which was desilylated to afford alcohol **5** after being pumped through a fluoride **4** loaded PASSflow reactor. The sequence was terminated by a reductive amination step in which the imine was generated in situ from ketone **5** with benzyl amine and the resulting solution was pumped through a microreactor loaded with borohydride to furnish amine **7** and small amounts of the corresponding diol.

In summary, we have developed a microreactor which can be incorporated into any conventional HPLC system. The key component is a novel monolithic composite material which is composed of a macroporous glass and a functionalized polymer. Changing the functionalization of the polymer allows various reactions to be efficiently performed in the flow-through mode. With this new reactor concept a cost-effective laboratory tool is available allowing easy flow-through applications in organic chemistry. This offers a high potential for automated polymer-assisted solution-phase synthesis.[12, 13]

Experimental Section

Preparation of polymer/glass monoliths and application in organic synthesis: Polymerization: vinylbenzyl chloride (45 g) and divinylbenzene (3.9 g; 65 % ethylbenzene) was dissolved in C14 – C17 *n*-paraffin (300 mL). After dissolution of azoisobutyronitrile (300 mg) porous glass rods with a diameter of 5.3 mm and a length of 110 mm were immersed in this solution. Air was removed from inside the pore volume by applying a vacuum for a short time. After heating at 70 °C overnight, the rods were cleaned of any adhering polymer and rinsed with trichloromethane.

Amination: The rods loaded with the polymer were covered with dry toluene and a continuous flow of trimethylamine was passed through this solution. After 4 days the rods were removed from the solution and dried in vacuo. Then, the rods, now functionalized with quarternary ammonium cations, were fitted with a casing and could be used as microreactors in organic synthesis.

Exchange with bromate(I) anions **2** and successive oxidation of **1**: The microreactor (chloride ion loaded) was treated with: deionized water (10 mL), sodium hydroxide solution (1 M, 10 mL), deionized water (10 mL), hydrobromic acid (2 M, 10 mL), deionized water (10 mL), methanol (10 ml), and dry dichloromethane (25 mL). After this procedure, a solution of 1.5 mmol diacetoxyiodinebenzene in dry dichloromethane (10 mL) was pumped through the reactor under argon in a recycle mode for one night.

After washing with dry dichloromethane (10 mL), the compound **1** (0.125 mmol) and a catalytic amount of TEMPO (0.1 mol%) in dry dichloromethane (10 mL) were pumped in a recycle mode under argon for 6 h through the reactor. The reactor system was rinsed with dichloromethane (10 mL) and the combined organic solvents were removed in vacuo and the residue was used for the further reactions without additional purification.

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[6] By employing monomers such as 4-vinylpyridine other polymers can be incorporated into the porous glass rod by precipitation polymerization.

[7] These studies were conducted as part of European-funded project at the center for NMR spectroscopy of the University of Wageningen (The Netherlands).

[8] Under these conditions, gel-type (Amberlite IRA 400) as well as macroporous (Amberlite IRA 900) anion-exchange resins loaded with borohydride anions, both of which are commercially available, behave similarly to the bare monolithic rod and the powdered material, respectively.

[9] Depending on the extent of polymer swelling caused by the solvent used the pressure drop was 10 bar (3 mL min^{-1}) and 28 bar (10 mL min^{-1}), respectively, across a length of the reactor.

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[11] For automation common HPLC equipment can be used (e.g. pumps, detectors, valves, dosing facilities).

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[13] The flow-through reactors presented are available from CHELONA GmbH (Potsdam).

An Analytical Approach for a Comprehensive Study of Organic Aerosols**

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Thorsten Hoffmann

Since the first scientific explanation of the so-called "blue haze" phenomenon above forests by Went,[1] the formation of natural organic aerosol particles in the atmosphere and their impact on the climate has drawn considerable attention. Airborne particles absorb, reflect, and scatter incoming solar radiation, play an important role in cloud droplet formation, and may even be involved in multiphase atmospheric chemistry.[2]

In recent reports it was established that especially the reaction of mono- and sesquiterpenes with tropospheric ozone contributes to the formation of organic aerosols,[3] however, our knowledge about reaction mechanisms leading to low-volatile products is still limited. Making things difficult is the fact that during the ozonolysis free OH radicals are formed that have to be considered.[4]

However, the initial steps of the terpene ozonolysis in the gas phase corresponds to known mechanisms,[5] exemplified in Scheme 1 for α-pinene **1**, the most abundant single monoterpene released by plants. The first step is the formation of the molozonide **2** that forms reactive Criegee intermediates **3a** and **3b**. Subsequent reactions lead to the formation of several low vapor-pressure products, such as pinonic acid (**4**), pinic acid (**5**), or hydroxy pinonic (**6**) acid which have been identified using mass spectrometric methods.[6] Although possible mechanisms for the generation of these carboxylic products have been suggested,[7] the overall understanding of the reaction mechanisms leading to condensable species is still inadequate.

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