



Catalyst assisted synthesis of initiator attached silica monolith particles via isocyanate-hydroxyl reaction for production of polystyrene bound chromatographic stationary phase of excellent separation efficiency



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ABSTRACT

Dibutyltin dichloride (DBTDC) was used as a catalyst to chemically bind 4-chloromethylphenylisocyanate (4-CPI) to porous monolithic silica particles via isocyanate-hydroxyl reaction, and the reaction product was reacted with sodium diethyldithiocarbamate (SDDC) to yield initiator attached silica monolith particles. Reversible addition-fragmentation transfer (RAFT) polymerization was taken place on them to result in polystyrene attached silica particles that showed excellent separation efficiency when packed in a chromatographic column (1.0 mm × 300 mm). The numbers of theoretical plates (N) of 56,500 is better than those of any commercially available HPLC or UHPLC column yet.

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1. Introduction

Modification of the surface of porous/nonporous inorganic materials by binding initiator moieties to their active sites followed by forming controlled polymer layers has been a well established strategy [1–6]. Such hybrid materials can be used as chromatographic stationary phases, and silica particles are the most versatile materials involved in surface modification for preparation of chromatographic media [7–19].

One of the trends of method development for better chromatographic performance has been the improvement of column efficiency by reducing particle size of stationary phase. It was initially in the 100 μm range and has been gradually reduced up to the sub-2 μm range [20–26]. There have been specially developed stationary phases such as core-shell particles, very fine porous particles, and monoliths for fast HPLC analyses and some recent review articles have been presented for their extensive introduction [26–29]. In view of separation efficiency of a column, core-shell particles have been regarded to be the best choice as stationary phase at present [26–28].

The detailed mechanism and applications of RAFT polymerization have been well introduced in the literature [11,12,30–35]. The critical feature of RAFT polymerization for chromatographic phases is preparation of surface-bound initiator by attaching a halogen terminated ligand to the silica surface followed by coupling an initiator moiety (Fig. 1). According to the RAFT polymerization mechanism, the polymer chain is grown in the C–S bond located between the spacer moiety and the diethyldithiocarbamate moiety (Fig. 1). However the stationary phases prepared in the past by RAFT polymerization had lower separation performance [11,12,14,15] in comparison to the conventional C18 phases. Preparation of ground silica monolith particles and their chromatographic application have been explored in our laboratory [36–38].

In this study, we report polystyrene bound partially sub-2 μm silica monolith particulate stationary phase with excellent separation efficiency and selectivity in HPLC. This study reports the highest N values for a column packed with a stationary phase based on silica particles.

Sodium diethyldithiocarbamate (SDDC) is bonded to silica surface as initiator entity after attaching 4-chloromethylphenylisocyanate (4-CPI) as a spacer (Fig. 1A). There have been some reports on catalytic effects of organometallic compounds for isocyanate-hydroxyl reaction in homogeneous systems [39–42]. The idea of using similar catalysts in a heterogeneous isocyanate-hydroxyl reaction has led us to carry out the reaction between 4-CPI

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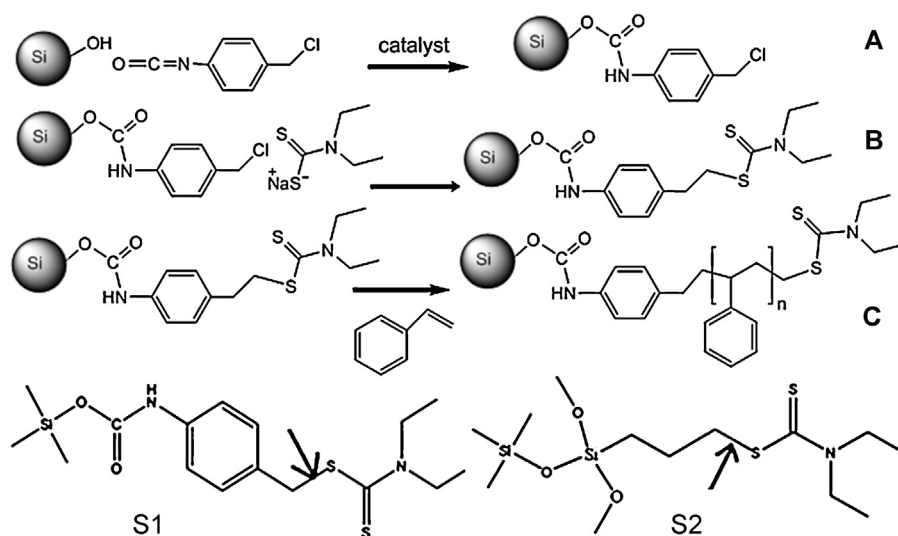


Fig. 1. Schematic pathways for synthesis of silica modified with chlorine-terminated ligand (A), initiator attached silica (B), and polystyrene bound silica (C), and the initiator silica structures prepared with 4-CPI (S1) and 3-chloropropyltrimethoxysilane (S2). The arrows denote the bond where the polymer chain is introduced and grown.

and silica silanol groups with some catalyst. Dibutyltin dichloride (DBTDC) was chosen for its good solubility in the reaction solvent.

The morphology of polymer layer attached on the porous silica particles was found dependent upon the chemical structure of the initiator ligand (spacer group + diethylthiocarbamate moiety), thus RAFT polymerization on the initiator attached silica (S1 in Fig. 1) prepared with 4-CPI without any catalyst yielded a polymer layer with some lumps of aggregated polystyrene [43] while RAFT polymerization on the initiator attached silica (S2 in Fig. 1) prepared with 3-chloropropyltrimethoxysilane yielded a polymer layer with little polystyrene lumps [44,45]. The formation of lumps was explained by the too rapid and uncontrolled polymerization owing to formation of too stable re-initiated radical species as in S1 compared to S2 [43–45]. Very recently, we have reported a column of excellent separation efficiency ($N \sim 50,000$) packed with polystyrene bound silica monolith particles prepared by a S2 type initiator [46].

We suspect that the S1 type initiator silica may produce a nice and uniform polymer layer without lumps if the density of the initiator ligand is high enough to cause simultaneous and uniform growth of polymer chains on individual initiator ligands followed by termination upon congestion of the grown chains. Thus catalyzed isocyanate-hydroxyl reaction was adopted here for such purpose. Even better chromatographic performance has been obtained in this study than that of Ref. [46].

2. Experimental

2.1. Materials

All the chemical reagents and solvents were of analytical grade and HPLC grade. Screen frits (1.6 mm diameter, 0.08 mm thickness, and 0.5 μm pore size) were purchased from Valco (Houston, TX, USA). Glass lined stainless steel tubing (30 cm, 1.0 mm ID, 1/8 in. OD) and silica capillary (50 μm ID, 365 μm OD) were obtained from Grace (Deerfield, IL, USA).

2.2. Synthesis of ground silica monolith particles (1)

Partially sub-2 μm porous silica monolith particles (1) have been synthesized by a renovated sol-gel procedure with multi-step heating followed by grinding and calcination according to the

method of Ref. [46]. Polyethyleneglycol (molecular weight 10,000) 1620 mg and urea 1650 mg were dissolved in 15 mL 0.01 N acetic acid in a Teflon vial, and magnetically stirred for 10 min in ice/water. Then, 5 mL tetramethoxysilane was added, and the mixture was kept under stirring for 40 min. The solution was incubated at 40 $^{\circ}\text{C}$ in an oven for 48 h then at 120 $^{\circ}\text{C}$ in an autoclave for 48 h. The residual water due to sol-gel process was decanted off and the solid cake of monolith was dried at 70 $^{\circ}\text{C}$ for 20 h, ground with mortar and pestle for 10 min, and calcined at 550 $^{\circ}\text{C}$ for 50 h.

2.3. Synthesis of initiator bound silica monolith particles

The mixture of 300 mg 4-CPI, 100 mg DBTDC, and 30 mL anhydrous toluene was stirred for 30 min in a 100 mL round bottom flask, and 820 mg **1** pre-dried at 120 $^{\circ}\text{C}$ overnight was suspended in it, and heated at 80 $^{\circ}\text{C}$ for 48 h. The product (**2**) was washed with anhydrous toluene and acetone (HPLC grade), filtered, and dried at room temperature in a vacuum desiccator overnight. SDDC 800 mg was dissolved in 30 mL anhydrous THF in a 100 mL round bottom flask, and the dried **2** (100 mL, RB flask) was suspended there under N_2 -purge for 10 min, and heated at 55 $^{\circ}\text{C}$ for 17 h under N_2 -purge. The product (**3**) was washed with THF, 60/40 methanol/water, and acetone, filtered, and dried at room temperature in a vacuum desiccator overnight.

2.4. RAFT polymerization of styrene

Styrene 5 mL dissolved in 25 mL anhydrous toluene was subjected to sonication for 10 min followed by N_2 purge for 20 min and 500 mg **3** was dispersed in it. Radical polymerization was carried out at 110 $^{\circ}\text{C}$ for 30 h under N_2 . The product (**4**) was washed with toluene at 110 $^{\circ}\text{C}$ and acetone at room temperature, filtered, and dried at 60 $^{\circ}\text{C}$ overnight.

2.5. Characterization

BEL-Japan (Osaka, Japan) BELSORP-Max was used to measure the BET/BJH nitrogen adsorption/desorption isotherms at 77 K, BJH pore sizes, and BET specific surface areas for the silica monolith particles and polystyrene bound silica monolith particles. The samples were out-gassed at 373 K for 10 h to obtain a residual pressure of less than 10^{-3} Torr. The amount of N_2 adsorbed at a relative pressure of $P/P_0 = 0.99$ was used to determine the total pore volume

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