

**SIMPLE SYNTHESIS OF SOME
CHROMATOGRAPHIC
STATIONARY PHASES BY THE
SOL-GEL METHOD**

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ABSTRACT

A simple method for the synthesis of some silicate-based polymers for use as chromatographic stationary phases is presented. Consecutive hydrolysis and polycondensation of some organically modified silicon alkoxides result in the formation of polymeric matrices in about 100% yield with high surface loading of organic moieties. The methyl, propyl, propylethylenediamine as well as other polymeric silicate derivatives were all prepared by this method. The use of the proposed procedure assures minimal residual surface hydroxyl group functionalities, thus avoiding the need for, usually low yield, multiple end-capping reactions. It was observed that the type of the catalyst and solvent used were important factors that influenced both the gelation time and gel transparency. The effect of these factors was dependent on the nature of the precursor under consideration and generalizations were not possible. The IR spectra of the synthesized polymeric matrices confirmed the formation of the desired product as well as the existence of very little of residual hydroxyl group functionalities.

INTRODUCTION

The evolution of high performance liquid chromatography (HPLC) as an important and widely spreading analytical technique necessitated an additional work towards the development of improved stationary phases capable of providing better separations. Knox [1] described the synthesis of a novel carbonized stationary phase by first filling the pores of the silica gel particles with a plastic monomer. Polymerization of the plastic monomer occurred, in situ, in the pores and carbonization takes place by heating the matrix at high temperatures where a surface of carbon on silica was obtained. Halasz and Sabastian [2] were the first to attach an organic group to the silica surface through the reflux of the silica gel particles with an aliphatic alcohol. However, it was soon realized that the Si-O-C linkage was easily hydrolyzed resulting in unstable stationary phases due to the gradual hydrolysis and regeneration of the silica gel. This instability was reflected as a change in the separation characteristics of these stationary phases with time. Therefore, attempts were devoted towards the synthesis of more stable preparations where Kirkland [3] succeeded to form the more stable Si-O-Si linkage by refluxing the silica gel particles with a chlorosilane derivative containing the desired alkyl chain. In the early seventies, Halasz and others [4-7] described an important procedure which involves the conversion of the hydroxyl groups on the silica gel surface into the chlorides, by refluxing with thionyl chloride, followed by coupling with Grignard reagent (RMgBr) to attach the R group (usually an alkyl chain) directly to the silicon skeleton. The Si-C bond is far more stable than either the Si-O-Si or the Si-O-C linkages. Using this approach, and changing the nature of the alkyl group (R) in the Grignard reagent used, stationary phases of different characteristics could be obtained. The synthesis of bonded phases thus described involved the reaction of the hydroxyl groups on the silica gel particles with some organic chemicals. Unfortunately, the reaction is far from being complete and large excess of residual hydroxyl groups will always be present. This requires additional steps of end-capping reactions, using trimethylchlorosilane as a common end-capping reagent.

Recently, there has been much interest of silicate based matrices prepared by the Sol-Gel process based on the hydrolysis and

polycondensation of alkoxysilanes or their derivatives. The possibility of low temperature polymerization of alkoxysilanes and the tailoring of their surface characteristics and porosity is a new dimension in the production of predesigned stationary phases for use in liquid chromatography [8-15]. Theoretically, maximum alkyl or functional group coverage (nearly 100% yield) as well as minimal residual surface hydroxyl groups should be expected from such an approach. This may be attributed to the need for all the hydroxyl groups for the formation of the three dimensional structure of the polymer and the presence of a 1:1 ratio of silicon atoms for each alkyl or functional group since each monomer contains one such group.

In this study, stationary phases of different characteristics are synthesized from their corresponding alkoxide derivatives by the Sol-Gel process. Effects of the different important factors on the hydrolysis and polycondensation of some alkoxide derivatives and the FTIR spectra of synthesized matrices will be presented.

EXPERIMENTAL

CHEMICALS AND REAGENTS

Tetraethoxysilane (TEOS), tetramethoxysilane (TMOS), methyltrimethoxysilane (MTMS), propyltrimethoxysilane (PTMS), aminopropyltrimethoxysilane (APTMS), vinyltriethoxysilane (VTES), trimethoxysilyl vinylbenzeneethylenediamine (TMSVBED) and trimethoxysilyl propylethylenediamine (TMSED) were purchased from Merck, Germany. Diaminobutane (DAB), triethylenetetramine (TETA), hydrochloric acid, sodium hydroxide, methanol, ethanol, 2-propanol, β -cyclodextrin (β -CD), and acetonitrile were obtained from Aldrich, USA. All solvents and catalysts were AR reagents while alkoxide precursors were GR reagents and were used as received without further purification. Distilled water was used throughout this study.

APPARATUS

The FTIR spectra were recorded using a PERKIN-ELMER FTIR instrument. All spectra were obtained using a KBr disc for each

sample which contained 1 mg of the sample per 100 mg of KBr. The KBr/sample mixture, after grinding, was subjected to a pressure of about 5 tons using a conventional hydraulic press. It was observed that drying of both the sample and KBr was essential for achieving good spectra as small amounts of water may cause erratic results. The pH of the different solutions were measured using a Hanna digital pH meter and an Orion combination glass electrode.

PROCEDURES

Entrapment of β -Cyclodextrin

The procedure for entrapment of β -CD in the silicate matrix involved mixing of 2mL of the alkoxy silane precursor with 1mL of ethanol followed by addition of 2mL of 0.05M NaOH containing 0.05 g of β -CD. The mixture was shaken for few seconds and left undisturbed in a fume hood to allow enough time for gelation depending on the type of precursor used. Only in the case of the TEOS precursor, the catalyst was a 2mL aliquot of 0.1M HCl saturated with β -CD since base catalysis was troublesome.

Self Condensation of MTMS and PTMS

Condensation of MTMS or PTMS involved mixing of 2mL of 0.05M NaOH with 1mL of the solvent followed by addition of 2mL of the precursor. In the case of MTMS, the mixture was shaken for few seconds and left undisturbed in a fume hood where gelation and increased self condensation occurred with time. However, gelation and self condensation of PTMS required sonication of the reaction mixture for about 2 hours before transferring to a fume hood.

Self Condensation of TMSED

Dropwise addition of water to TMSED precursor resulted in an immediate formation of a yellow solid and transparent gel without the use of a catalyst. A 1:1 water: precursor mole ratio was sufficient for the formation of the solid gel. However, a 1:2 water:precursor mole ratio promoted partial hydrolysis and a sol was obtained.

Cross Condensation of TMSED and Pentanal

Initially, a TMSED sol was prepared by careful addition of about 0.2mL of water to 0.02 mol of TMSED with sonication. Then, 0.02 mol of pentanal were added dropwise with sonication. The solid gel was obtained immediately where no catalyst or solvent was necessary.

Preparation of the Sample for IR Analysis

Each sample was finely grinded, washed with plenty of distilled water, and finally with methanol. The sample was dried in an oven at about 100 °C for 4 hours and then carefully transferred to a desiccator. Predried and desiccated KBr was also used in the preparation of the KBr disc which contained about 1% of the sample and subjected to a pressure of 5 tons for 1 min.

RESULTS AND DISCUSSION

Acid versus Base Catalysis

The nature of the catalyst used was found to have an important influence on both the gelation time and gel transparency. It was observed, for instance, that using an acid catalyst of any concentration lower than 2M for the polycondensation of PTMS resulted in partial condensation only. A thick, viscous, and transparent glue-like product was always obtained with acid catalysis of PTMS. However, using a base catalyst for the polymerization of PTMS resulted in the production of fine white particles. Another important, but expected, result was observed in the polycondensation of TMSED where no catalyst was necessary. The polycondensation of TMSED in absence of a catalyst could be attributed to the presence of the amine moiety as part of the alkoxide monomer which evidently can drive a base catalysis route. Therefore, it is clear from the arguments above that the acid/base catalyst should optimally be selected in order to achieve the desired product. The gelation time for the TEOS precursor was significantly decreased as the acid concentration was increased. However, in the case of PTMS and VTES precursors no change in the gelation time with catalyst concentration was observed (Table I). It could be justified to conclude that the catalyst type and concentration has some influence on the gelation time and gel formation in the case of some alkoxide precursors but this ultimately depends on the type of precursor under consideration.

Effect of Solvents on Gelation Time

In most cases, addition of a solvent is desired in order to improve the mixing and miscibility of the different reagents involved in the Sol-Gel process. Alkoxysilane precursors are usually immiscible with water due to the organic moiety of metal alkoxides. It was observed that the nature of the solvent used has pronounced

influence on the gelation time. This can be shown by comparing the gelation times of some precursors in presence of solvents. It was observed that addition of 1mL of ethanol to 2mL of the TMSED precursor followed by 2mL of 0.05M NaOH solution resulted in no gel formation, even after days of reaction. However, excluding ethanol from the reaction mixture resulted in the formation of a clear yellow gel within two minutes. Also, a significant change in gelation time as a function of solvent type was observed in the case of the MTMS precursor where mixing of 2mL of MTMS with 1ml of ethanol and 2mL of 0.05M NaOH, as a catalyst, resulted in the formation of a nontransparent gel after about 45 min. However, performing the same experiment in absence of ethanol forced the formation of a transparent gel within two minutes. Fast gelation times were also achieved in presence of solvents, other than ethanol, like 2-propanol, acetonitrile or methanol where gelation times of 3-5 min. were achieved. This may be attributed to a possibility of methoxy/ethoxy exchange in presence of ethanol where it is much easier to hydrolyze the methoxy derivative. Also, it should be easier to hydrolyze the isopropoxy rather than the ethoxy derivative. Acetonitrile seems to act as an inert solvent leading to gelation times comparable to those obtained in absence of solvents. Table II summarizes the effects of solvents on both gelation time and gel transparency.

Entrapment of β -Cyclodextrin into a Silicate Matrix

Successful attempts to use the Sol-Gel method for the entrapment of several species were reported in the literature [16-20]. Most of this work has been focused on the study of the change in the characteristics of the entrapped species in the immobilized state, but none described an entrapment matrix for use in liquid chromatography. Appreciation of the importance of β -CD in chromatographic separations is well documented. This compound is a major mobile phase additive in separation of chiral compounds. Several alkoxide precursors and catalyst conditions were used in order to study the entrapment of β -CD into a solid matrix by the Sol-Gel process. The importance of this stems from the potential possibility of reducing the cost of chiral separations and provide a route for a new technology for tailoring of stationary phases. Also, it should serve as a model for the simple preparation of stationary phases of other

characteristics by entrapment of specific chemical and biochemical species. MTMS and TMOS were the best precursors for the fast entrapment of β -CD where gelation occurred within 5 min., without sonication, using a 1:1:2 volume ratio of precursor:base: ethanol. The catalyst contained a 0.05M NaOH solution in which β -CD was dissolved. The TEOS entrapment of β -CD was successful only using acid catalysis and in presence of ethanol. In all cases described above, a homogeneous gel containing entrapped β -CD was always obtained. It was interestingly observed that TMSVBED expelled the β -CD to the bottom and attempts to entrap this compound in that matrix failed. Other useful precursors, but with longer gelation times, included APTES and PTMS both in basic conditions and in presence of ethanol as a solvent.

Synthesis of Methyl and Propyl Terminated Stationary Phases

The methyl and propyltrimethoxysilane precursors were used for the preparation of stationary phases containing methyl and propyl groups directly attached to silicon. This was accomplished by self condensation of each precursor under suitable conditions. It was observed that the polycondensation of both precursors failed in presence of an acid catalyst where partial gelation of MTMS and a viscous, glue-like, solution of partially polymerized PTMS was only achieved. However, switching to a base catalyst (0.05M NaOH) and in presence of an organic solvent such as methanol, 2-propanol, or acetonitrile resulted in an excellent system where gelation of MTMS occurred within 5 min. However, gelation times of about 45 min were recorded when ethanol was used as the solvent. This gelation time, in presence of ethanol, is much greater than that needed for the same precursor but in presence of β -CD as mentioned earlier. This behavior may indicate an important catalytic role of β -CD in the acceleration of MTMS polymerization which may be attributed to better orientation of the precursor molecules in presence of β -CD.

The self condensation of PTMS was best achieved using a base catalyst and in presence of ethanol or acetonitrile as a solvent. The result of the polymerization reaction, performed under sonication conditions, was a nontransparent white solid after about 2 hrs. The longer time needed for PTMS polymerization could be due to the

presence of the propyl group which retards the condensation reaction as the rate of condensation seems to be a function of the alkyl chain length [21]. The yield of the polycondensation reaction of both MTMS and PTMS was the same as the theoretical yield when a polymer having a repeating unit as the structure shown in Scheme I was assumed. In addition, other successful catalysts for the polymerization of PTMS included TETA as well as DAB where gelation times shorter than 10 min. were achieved using a mole ratio of 1:0.01:6:6 of precursor: catalyst:water:methanol, respectively. The resulting polymer was finely powdered, successively washed with distilled water and methanol, and finally examined by FTIR as described in the procedures section. Figure 1 shows the IR spectrum of polymerized TEOS (lower) and Polymerized PTMS (upper). It is clear from the figure that the stretching vibrations due to the surface O-H groups at about 3500 cm^{-1} disappeared in polymerized PTMS when compared to the spectrum of polymerized TEOS indicating minimal presence of such O-H groups in the polymer. Also, bands at about $2800\text{-}3000\text{ cm}^{-1}$ due to C-H stretching vibrations appear due to presence of the propyl group.

Synthesis of Ethylenediamine Terminated Stationary Phases

It was interestingly observed that TMSED formed a polymer directly upon addition of excess water and with full exclusion of a catalyst or a solvent as required by other types of precursors. Moreover, addition of ethanol was found to abort the self condensation reaction even in presence of 0.05M NaOH as a catalyst. It is believed that the condensation reaction proceeds in absence of a catalyst due to the basic nature of the amine groups present in the monomeric skeleton of the precursor which may also explain the high speed of the polymerization reaction. The solid gel formed is yellow in color and completely transparent. Figure 2 shows the IR spectrum of the TMSED polymer where the N-H stretching vibrations could be located at about 3400 cm^{-1} .

A completely different result was observed when TMSED was added stepwise to a great excess of water (1:50 mole ratio of precursor:water) with sonication. No gel was obtained but rather a viscous sol which, upon keeping in an oven at $50\text{ }^{\circ}\text{C}$ for several days, resulted in a noncrackable material. The resulting material looked like

a thick membrane at the internal surface of a scintillation glass vial. We recommend this procedure if a film of TMSED, rather than particulates, polymer is desired.

Also, chemical modification of TMSED before polymerization was attempted. A 1:1 mole ratio of TMSED:pentanal was mixed without solvents or catalysts. It was observed that the aldehyde condenses to the amine group of TMSED in an exothermal reaction forming the C=N linkage. It is well known that water is the result of such a polymerization reaction. The released water from the condensation reaction partially hydrolyze TMSED, and this leads to significant polymerization. The resulting polymer lacks the amine terminal which could be clearly seen from Figure 3 where the peak at about 3400 cm^{-1} was significantly diminished.

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Figure 1: The IR spectrum of polymerized TEOS (lower) and polymerized PTMS (upper).

Figure 2: The IR spectrum of polymerized TMSED.

Figure 3: The IR spectrum of TMSED/pentanal polymer.

Table I: Effect of acid/base catalysis on gelation time for some alkoxide precursors

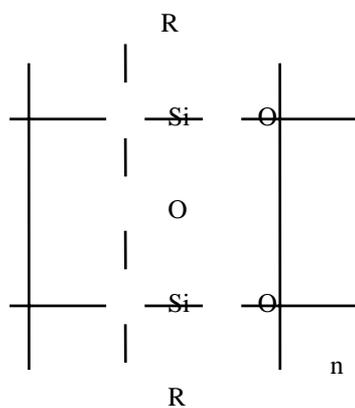
Precursor	Acid Concentration, M	Base Concentration, M	Gelation Time
VTES	0.30	-	2 days
VTES	0.90	-	2 days
TEOS	0.75	-	2 hrs
TEOS	2.0	-	1 hr
TEOS	0.05	-	24 hrs
PTMS	1.0	-	No gelation
TEOS	-	0.05	6 days
TMOS	-	0.05	5 min
PTMS	-	0.025	2 hrs*
PTMS	-	0.05	2 hrs*
PTMS	-	0.075	2 hrs*

* In presence of a 1:1 (v/v) ratio of precursor to ethanol

Table II: Effect of some solvents on gelation time and gel transparency

Precursor	Catalyst, M	Solvent	Gelation Time	Transparency
TMOS	0.05	Methanol	5 min	T
TMOS	0.05	-	No gelation	-
TEOS	0.05	Ethanol	No gelation	-
TEOS	0.05	Methanol	3 hrs	NT
TMSED	0.05	Ethanol	No gelation	-
TMSED	0.05	-	<2 min	T
MTMS	0.05	Ethanol	45 min	NT
MTMS	0.05	-	2 min	T
TMOS	0.05	Ethanol	5 min	T
TMOS	0.05	Methanol	5 min	T
TMOS	0.05	2-Propanol	5 min	T
TMOS	0.05	Acetonitrile	5 min	T
TEOS	2.5	-	2 hrs	T
TEOS	2.5	Methanol	24 hrs	T
VTES	2.5	-	2 hrs*	T
VTES	2.5	Metanol	2 days*	T

* Partial gelation was achieved. T stands for transparent and NT stands for nontransparent



Scheme I: The repeating unit of the alkyl terminated siloxane polymeric matrix. R stands for methyl or propyl derivative.