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SYNTHESIS OF CHEMICALLY BONDED POLYSTYRENE-DIVINYLBENZENE ON SILICA BY FREE RADICAL INITIATION WITH GAMMA RADIATION CROSS-LINKING

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ABSTRACT

A procedure is described for direct chemical bonding of polystyrene-divinylbenzene (PS-DVB) to silica. The method is a two-step process which first bonds and polymerizes the material via peroxide initiation in the presence of azobisisobutyronitrile (AIBN). The second step involves cross-linking the bonded polymer by gamma irradiation. The success of the procedure is evaluated by carbon-hydrogen analysis and DRIFT spectroscopy of the product. Chromatographically the bonded material is tested by separations of alkylarylketones.

INTRODUCTION

The use of silica-based materials, particularly those referred to as reversed phase packings, are very effective for separation of small acidic or neutral compounds in the pH range of 2 - 7. Many molecules, especially those which are at least partially ionized, may be retained by residual silanols as well as the bonded organic phase. Raising the pH of the mobile phase to decrease peak asymmetry caused by surface adsorption may lead to dissolution of the packing.

A number of alternate methods have been devised to improve peak symmetry. An ion-pairing reagent can be used to form a neutral complex (1,2) which prevents the charged analyte from adsorbing on the surface. A base can be

added to the mobile phase (3) which will compete with the solute for the residual silanol sites. Operation at high pH can be accomplished by use of a silica saturator column (4,5) to suppress dissolution of the support material.

Another approach is to substitute a polymeric packing such as polystyrene-divinylbenzene (PS-DVB) for silica-based materials. However polystyrene is: very hydrophobic which can be a particular problem for macromolecules; susceptible to swelling and shrinking when solvents are changed; and prone to column packing difficulties (6). Yang and Verzele (7) have recently described a new type of modified polystyrene that is more compatible with aqueous mobile phases. Another possibility is to produce a polymer in the presence of silica (8) so that the stationary phase is physically adsorbed on the solid support. This process will retain some of the advantages of both the silica and the polymeric packing such as rigidity, peak symmetry, etc., but may not eliminate all of the difficulties such as pH stability, hydrophobicity, etc. A third possibility is to chemically bond a cross-linked polymer to the surface of silica. Such a process could further inactivate the surface by reaction of the silanols as well as provide increased rigidity to the polymeric structure. This paper describes a method for chemically bonding as well as polymerizing styrene and divinylbenzene on silica and then cross-linking the bonded material by gamma irradiation.

MATERIALS

The silica support used was 10 μm Lichrosorb (EM Science, Gibbstown, N.J.). Styrene and divinylbenzene monomers (Fluka, Ronkonkoma, N.Y.), AIBN (azobisisobutyronitrile) and di-tertbutylperoxide (VWR, Sunnyvale, CA) and alkylarylketone standards (Pierce Chemical, Rockford, Ill.) were either reagent grade or the highest purity available. All chromatographic solvents (American Scientific, Santa Clara, CA) were HPLC grade. Other solvents for reactions and clean-up procedures were reagent grade.

METHODS

Twelve grams of silica particles were dispersed into 60 mL of a 3% (w/v) solution of di-tertbutylperoxide in toluene. The mixture was then transferred to a 2L Morton flask equipped with a paddle blade stirrer. An additional 200 mL of toluene was added to the mixture, agitated and then sparged with argon for 30 min. Four and one-half mL of styrene and 0.15 mL of divinylbenzene which had been previously degassed were then added to the flask and stirred for 20 min (70^o). After 4 h a second portion of monomer (0.15 mL of

divinylbenzene) was added which was followed after 15 min. by 0.1 g of AIBN. After reacting for 7.5 h at 70° the product was extracted with a Soxhlet apparatus and washed with 50 mL of toluene, 100 mL of methanol, 100 mL of 1:1 methanol/water, and finally 100 mL of methanol. The product was dried under vacuum and then stored in a dessicator.

The irradiation was done by a standard electron linear accelerator utilizing high energy x-rays produced by bremsstrahlung, a nondestructive technique for isotope replacement. The sample was irradiated at a peak energy of 6 Mev with an x-ray output measured at 1500 rads/min at 1 meter from the source. The material was packed in 3 two mL test tubes in order to ensure uniform irradiation and was exposed continuously for 18 hours. The total dose of the exposure was 1.6 megarads.

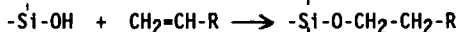
After irradiation, the product was packed into a 300 x 4 mm i.d. stainless steel column by a standard Haskell pneumatic amplification pump using acetone as the packing solvent. Alkylarylketone separations (9) were done at 35° using 40:60 water-methanol for 5 min. followed by a linear gradient to 100% methanol in 15 min. at a flow rate of 1.5 mL/min. The sample size was 10 μ L of 0.05% (w/v) of each compound in 75:25 methanol-water.

Chromatographic experiments were performed on a Varian 5020 liquid chromatograph equipped with a UV-100 detector. Samples were introduced by means of a Rheodyne (Cotati, CA) 7125 injector valve. IR spectra were obtained in the diffuse reflectance mode (DRIFT) on a Perkin-Elmer Model 1800 spectrometer.

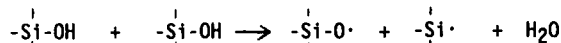
RESULTS AND DISCUSSION

An initial attempt to make chemically bonded PS-DVB via a single step reaction in which cross-linked styrene-divinylbenzene was added to a hexane solution of dispersed silica in the presence of AIBN was unsuccessful. Even though bonding of the polymer via free radical addition might be possible, it did not occur under these reaction conditions. Instead the resulting product analyzed by a DRIFT spectrum contained only akylated and not aromatic material bonded to the silica. Apparently some type of cleavage reaction occurred without bonding of the polymer to silica.

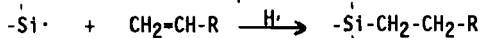
Although a possible alternative might be bonding via an organosilane reagent (10-13), a second attempt was made using peroxide initiation. In this process the styrene monomer is attached to the surface in the presence of t-butylperoxide which forms a polymer radical. Actual attachment of the organic material through free radical addition could occur in one of two ways. First there could be hydrogen abstraction which results in a silicon-oxygen-carbon.



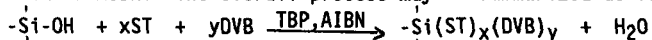
While this reaction would temporarily create a bond between the polymer and the silica surface, any contact with water would quickly hydrolyze this bond. Another possibility is the formation of both $\text{Si-O}\cdot$ and $\text{Si}\cdot$ radicals on the surface.



Such a mechanism has been shown to occur on silica (14) in the formation of hydrides (15,16). This process might be even more favored when the two hydroxyls are geminal. The second step would then be



Very few such attachments would be necessary to form a bond that would survive subsequent treatment with water and permanently fix the polymer to the surface. In addition, a small amount of the intermediate and the final product (after irradiation) were subjected to several washings with THF. No change in the DRIFT spectra of either material was observed after this treatment. Therefore, a range of solvents were unable to displace the organic material from the surface lending further support to the existence of a chemical bond between the polymer structure and the silica surface. Further polymerization occurs with the addition of the divinylbenzene and the free radical initiator AIBN. The overall process may be summarized as follows:



where ST is styrene, DVB is divinylbenzene, TBP is t-butylperoxide, and $x \gg y$. This preliminary product was then irradiated which resulted in the formation of radicals leading to the final cross-linked material. The dose chosen was shown previously to have caused no radiation damage to cross-linked PS-DVB beads (17).

The results of both the initial bonding reaction and the cross-linking process can be monitored by DRIFT spectra. The most important spectral regions for these two materials are shown in Fig. 1. Both the $3200 - 2700 \text{ cm}^{-1}$ and the $2100 - 1300 \text{ cm}^{-1}$ regions indicate that the initial reaction was successful and the irradiation procedure then lead to noticeable changes in the spectrum. Fig. 2 is a comparison of the spectra of the final product to cross-linked PS-DVB beads. Since the two spectra are virtually identical, there is no doubt that the material on the silica is cross-linked PS-DVB.

The possibility that the product is not bonded to the silica but merely polymerized around it must be considered. Because the material was extensively washed in a number of solvents before cross-linking without any apparent loss of organic phase as determined by DRIFT analysis, it is unlikely that the initial product was merely adsorbed on the surface. An examination of the DRIFT spectrum of a carefully dried sample (18) shows that free silanol stretch has been reduced in intensity and shifted from 3741 cm^{-1} to 3737 cm^{-1}

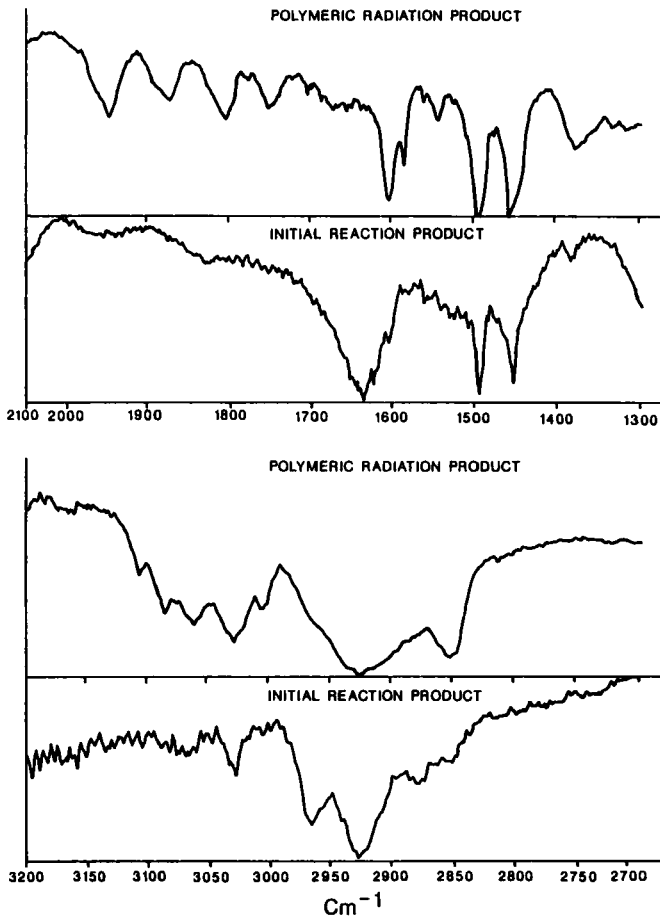


FIGURE 1. DRIFT spectra of initial reaction product and polymeric radiation product in the 2100 to 1300 cm^{-1} (top) and 3200 to 2700 cm^{-1} spectral regions.

in both the intermediate and product materials. This result is consistent with previous work (18) describing similar changes in the infrared spectrum of silica as the number of unbonded SiOH groups diminishes.

Carbon-hydrogen analysis of the bonded cross-linked polymer yielded the following results: C = 12.44% and H = 1.31%. The following formula (19) can be used to calculate bonded phase coverage(BPC):

$$\text{BPC } (\mu\text{mole}/\text{m}^2) = 10^6 \times \%C/[1200N_C - (\%C)(M-1)]S$$

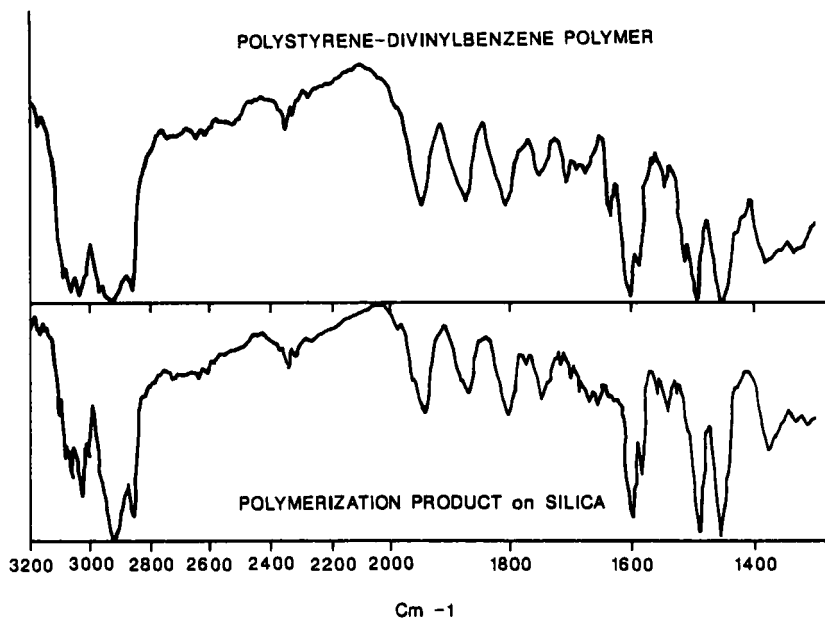


FIGURE 2. DRIFT spectra of cross-linked PS-DVB polymer beads (top) and polymerization product on silica (bottom).

where N_C is the number of carbon atoms, M is the molecular weight of the bonded material, and S is the surface area of the silica. If it is assumed that $N_C = 10$, $M = 132$, and $S = 320 \text{ m}^2/\text{g}$, then the value obtained from the above formula is 3.75 umole/m^2 . Such a value would be comparable to the best values obtained from a C-10 moiety (20) if a single cross-linked unit were attached at each silanol group. This seems unlikely so an exact quantitative determination of the number of reacted silanols is not possible from this analysis. However, these results suggest that approximately a monolayer coverage occurs.

Fig. 3 shows a chromatogram for the separation of a mixture of alkylarylketones. This homologous series has been shown to be useful for characterizing the retention properties of stationary phases (9, 21-23), especially those that possess reverse phase characteristics. If one plots $\log k'$ vs. carbon number the usual linear graph for reverse phase behavior is not obtained when done isocratically. The relatively long retention of the lower members of the series is probably due to strong pi-pi interactions between the

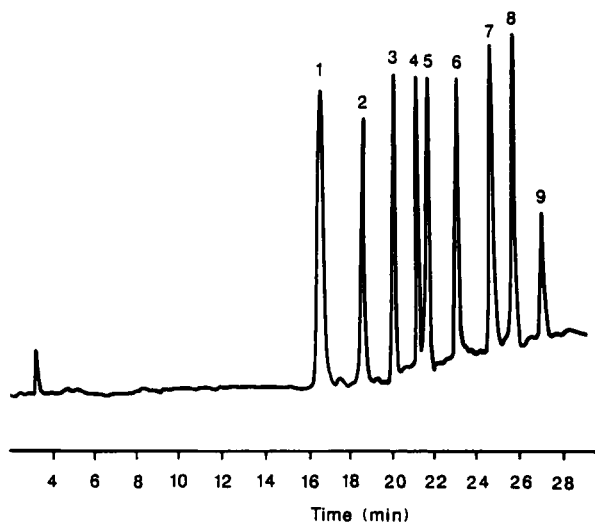


FIGURE 3. Separation of alkylarylketones on PS-DVB silica. Mobile phase: 40:60 methanol-water for 5 min. followed by a linear gradient to 100% methanol in 15 min. 1, acetophenone; 2, propriophenone; 3, butyrophenone; 4, valerophenone; 5, hexanophenone; 6, octanophenone; 7, decanophenone; 8, laurophenone; 9, myristophenone.

solute and the stationary phase. As the alkyl chain gets longer there is no further increase in the pi-pi interaction but there is an increase in the hydrophobic interaction.

In conclusion, it remains to be seen whether a stationary phase which is a totally organic polymer, or a polymer adsorbed on silica, or a polymer bonded to silica will prove to be the most useful chromatographically. It is likely that all three will have advantages for certain types of separation problems. Such a conclusion must await a more detailed comparison of these three phases so that chromatographic efficiency as well as durability, solvent effects, etc. can be evaluated. A more detailed study of these factors as well as alternate bonding methods is currently underway.

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