

Graft Polymerization of Vinyl Acetate onto Silica

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SYNOPSIS

A method is reported for the surface grafting of polyvinyl acetate (PVAc) onto modified, nonporous silica. The silica surface was modified by silylation with vinyl(triethoxy)silane followed by graft polymerization of vinyl acetate. The graft yield was measured by thermogravimetric analysis and the monomer conversion was monitored by UV spectral analysis. The rate of the graft polymerization and the graft yield were proportional to the initial monomer concentration. Vinyl acetate conversion followed first-order kinetics and displayed a trend of increasing initial rate with increasing monomer concentration.

INTRODUCTION

Inorganic oxide surfaces can be modified by chemical treatment to obtain desired interfacial properties for a variety of applications. One such chemical treatment is modification with polymers. Polymers can be adsorbed or grafted to inorganic oxide surfaces for use as fillers in composite materials,¹ chemically bonded support packings for liquid chromatography,²⁻⁴ and for gas chromatography,⁵ in the study of colloid stability,⁶ in biocompatible gels,⁷⁻⁹ and for the immobilization of enzymes.¹⁰ In all cases the proper selection of the polymer, along with control of the molecular weight and the density of the grafted chains, is needed to obtain the desired properties of the polymer-grafted particles.

Graft polymerization is the process of growing macromolecules from a reactive site that is covalently bonded to the surface. Polymer grafting, in contrast, is the process of attaching living polymer chains to reactive sites on polymers¹¹ or other surfaces. Graft polymerization onto inorganic oxides, involving the modification of the particle surface either for bulk free-radical polymerizations,^{3,6,12-14} anionically initiated polymerizations,^{6,15-18} or by free-radical polymerizations with the initiator bound to the surface,^{1,6,10,19} have all been reported in the literature. Free-radical graft polymerization yields

a molecular weight distribution of the grafted chains that is characteristic of bulk free-radical polymers.^{19,20}

Free-radical graft polymerization onto silica requires that the surface is modified by bonding reactive sites—either initiator or reactive functional groups—to the silica. The surface modification can be achieved, for example, with organosilanes.^{2,12,20-23} A schematic representation of the bonding of a vinylsilane to hydroxylated silica is shown in Figure 1. The covalent bonding of silanes with the general formula RSiX_3 where X represents a hydrolyzable group such as methoxy or ethoxy and R represents a nonhydrolyzable alkane, alkene, or aromatic group has been reported by numerous investigators.^{5,6,10,23-27}

In this article we report the free-radical graft polymerization of polyvinyl acetate (PVAc) onto nonporous silica that has been modified with vinyl(triethoxy)silane. Many of the low molecular weight chlorinated hydrocarbons are good solvents for PVAc, such as chloroform.²⁸ Thus, a resin with a surface-bound PVAc layer should be of interest for reverse-phase liquid chromatography of chlorinated hydrocarbons. Polyvinyl acetate is readily converted into polyvinyl alcohol by complete alcoholysis of the pendant acetal group, or into PVAc-PVA copolymers by partial alcoholysis of the acetal groups.^{29,30} Thus, the graft polymerization of PVAc may be of interest for composites where a bonded polymer layer of PVAc-PVA copolymer would offer a wide range of polarity and a wide range of com-

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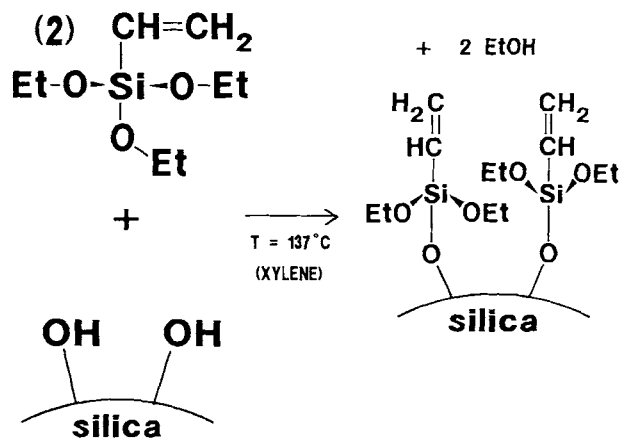


Figure 1 Vinylsilylation of hydroxylated silica.

patibility with various solvents, depending on the composition of the copolymer.

EXPERIMENTAL

Graft polymerization of PVAc onto nonporous silica was accomplished in a batch slurry reactor. The grafting reaction was carried out with silica particles modified with vinyl (triethoxy) silane. The free-radical polymerization at the surface vinyl group resulted in polymer chains covalently bonded to the surface of the silica. Ethyl acetate was chosen as the solvent because it was a good solvent for the monomer (vinyl acetate), the polymer, and the initiator. The progress of the reaction was monitored by ultraviolet spectral analysis of the polymer-monomer solution, and the grafted polymer yield was determined by thermogravimetric analysis (TGA) of the silica particles.

Materials

Nonporous silica (Novacite L207-A) with a mean particle size of $5\ \mu\text{m}$ was provided by Malvern Minerals Co. (Hot Springs, AR). Vinyl acetate monomer and the initiator [α,α' -azobis(2,4-dimethylvaleronitrile)], both reagent grade, were obtained from Polysciences Corp. (Warrington, PA), while the vinyl (triethoxy) silane used in the silylation reaction was reagent grade purchased from Petrarch Systems (Bristol, PA). Ethyl acetate, used as the solvent in the reaction mixture and for washing the grafted silica, and methanol and acetone, used for grafted silica washing, were spectrophotometric grade and received from Fisher Scientific (Tustin, CA). Cyclohexane, used as the diluent for the UV analysis, was spectrophotometric grade while mixed xylenes

were certified A.C.S. grade (Fisher Scientific, Tustin, CA).

Silylation

The silylation procedure followed the procedure of Chaimberg et al.¹² and Chaimberg and Cohen.²⁰ The novacite silica was converted to its hydroxylated state by washing batch-wise with strong acid. A batch of approximately 50 g of novacite was stirred in 500 mL of 0.12M HCl solution for 24 h. The acid slurry was then vacuum filtered and washed with distilled, deionized water until the filtrate pH was no longer acidic. This washed novacite was air-dried for 5 days and then dried under vacuum for 1 day at 150°C . The hydroxylated silica was kept at 150°C under vacuum until the start of the reaction. Vinylsilylation was carried out in a 500-mL batch slurry reaction in a 10% (v/v) solution of vinyl (triethoxy) silane in mixed xylenes.²⁶ The reaction mixture was stirred vigorously and maintained at the boiling temperature of the solution for 8 h. The temperature of the condenser was kept above 80°C to drive off the ethanol produced from the bonding of the vinylsilane to the silica.¹² The resulting silica slurry was filtered through a Teflon membrane ($1.0\ \mu\text{m}$ pore diameter) and washed with 2 liters of xylene and allowed to cure at 50°C under vacuum for 24 h.³¹ The replacement of the remaining ethoxy groups by hydroxyls was achieved as described in Figure 2. The silylated silica was subsequently washed exhaustively with distilled, deionized water, air-dried in a suction flask, and then oven-dried at 105°C under vacuum in preparation for graft polymerization.

Graft Polymerization

The graft polymerization reactions at 60°C were performed in a jacketed reactor under a nitrogen atmosphere (see Fig. 3). The nitrogen atmosphere

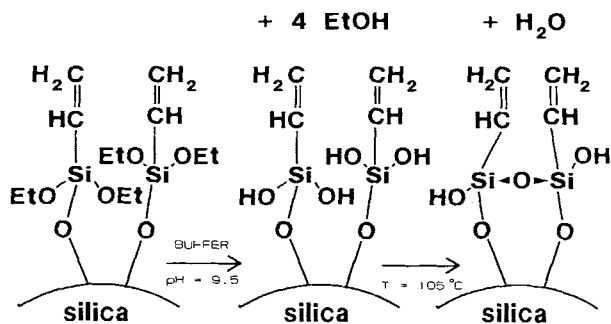


Figure 2 Silane alcoholysis and condensation on silica surface.

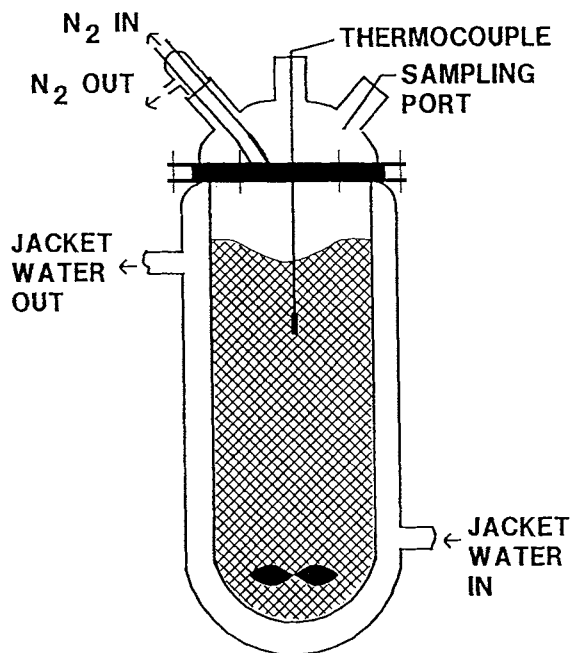


Figure 3 Slurry reactor for graft polymerization.

was necessary to exclude oxygen, which promotes the formation of acetaldehyde, a known chain-transfer agent.^{32,33} The reactions were carried out at 60°C in an ethyl acetate solvent at initial vinyl acetate concentrations of 10, 25, and 40% (v/v). Ethyl acetate is a good solvent for the monomer, the polymer, the initiator, and the vinyl-modified silica; thus, it allowed for better mixing and eliminated the possibility of a lag time in reaction at the surface due to improper wetting of the silica particles. The initiator, α, α' -azobis(2,4-dimethylvaleronitrile) was used at an initial concentration of 0.0279M based on the work of Ito.³⁴ In all cases the reaction was allowed to proceed for about 10 h.

The graft polymerization procedure consisted of first adding the vinylsilylated silica and solvent to the temperature-controlled reactor with vigorous stirring until the reaction mixture reached the desired temperature. Subsequently, the monomer was added followed immediately by the initiator. Slurry samples of 5 mL volume were taken from the reactor at various times and centrifuged at 10,000 rpm for 2 min in a centrifuge (IEC Centra 4b, International Equipment Co., Needham Heights, MA) to separate the silica particles from the solution. The filtered, grafted silica samples were immediately washed with 100 mL of ethyl acetate, methanol, and acetone over a 1.0- μm polyester filter on a fritted glass funnel. It was found that washing the grafted silica samples with the three solvents was sufficient for removing

any homopolymer that may have adsorbed. In addition, a blank grafting reaction with unmodified silica revealed that the amount of polymer adsorbed onto the surface of the particles during the reaction was negligible.

The polymer graft yield was determined by TGA. The amount of grafted polymer was determined by the difference between the weight loss of the sample at 700°C and the weight loss of the vinyl-modified silica at the same temperature. All TGA samples were held at 100°C until no further weight loss was noticed for 10 min before heating at a rate of 25°C/min to 700°C, a temperature sufficiently high to remove all of the bonded silane.¹²

The monomer concentration in the reaction mixture was determined from UV analysis (8452a Diode Array Spectrophotometer, Hewlett-Packard, Palo Alto, CA). An appropriate dilution factor in cyclohexane was used such that the absorbance was below 1.6 (i.e., a transmittance greater than 20%). The ester group has an absorption maximum at 218 nm, whereas the absorption maximum for vinyl acetate diluted in cyclohexane is at 197 nm. The dilution factor required for ethyl acetate was about 200 times less than that for vinyl acetate since the vinyl group absorbs at a wavelength of 198 nm much more strongly than the ester group absorbs at 217 nm. The extinction coefficients are reported in Table I. Monomer conversion was defined as

$$\text{Conversion} = \frac{[\text{monomer}]_{t=0} - [\text{monomer}]_t}{[\text{monomer}]_{t=0}}$$

where from Beer's law, $[\text{monomer}] = \text{absorbance (at 198 nm)} / (\epsilon l)$. The amount of monomer consumed in the formation of the grafted polymer accounted for less than 0.05% of the total monomer consumed in the reaction. Therefore, the contribution of grafted polymer to the calculated monomer conversion in the bulk solution was negligible.

In order to determine the extent of polymer adsorption that may have occurred during the reaction, a limited number of PVAc adsorption studies (at

Table I Wavelength of Absorbance Maximum and Extinction Coefficients for Vinyl Acetate and Ethyl Acetate

Species	Solvent	ϵ at 198 nm (L/mol cm)
Vinyl acetate	Cyclohexane	7.77E+3
Ethyl acetate	Cyclohexane	42.6

22°C) were carried out. Two different molecular weights of polymer were used (90,000 and 500,000) to assess the potential adsorption of PVAc onto the unmodified and vinylsilylated silica. The adsorption studies were done in 14-mL vials sealed with Teflon-lined screw-cap tops. Carefully weighed quantities of silica were mixed with an accurately measured aliquot of polymer solution and rotated end over end for an equilibration period of one week. Blanks (silica and solvent, no polymer) and controls (polymer solution, no silica) were run concurrently. No detectable amount of polymer adsorbed onto the control vials. The amount of adsorbed polymer was determined from knowledge of the initial and final PVAc concentrations that were measured with a refractive index monitor (Model 1750, Bio-rad, Cambridge, MA).

RESULTS AND DISCUSSION

The surface silylation results (Table II) obtained by TGA indicated a surface concentration of between 23 and 26 vinyl units/nm² (32 to 40 μmol/m²). An example of the TGA of a vinylsilylated silica sample is shown in Figure 4. Graft yields as high as 3 mg PVAc/m² silica were obtained. Surface hydroxyl concentrations for silica are reported between 4.6 and 9.0—OH/nm².³⁵ Thus, the silylation method employed in the present study resulted in the bonding of approximately 3–5 vinyl groups for each

available surface hydroxyl group. This high degree of silylation indicates a multilayer coverage due to the polycondensation of the ethoxy groups on the silica surface.²⁰ In contrast to the organic phase silylation method, aqueous silylation results in a surface vinyl concentration between 0.05 and 2.1 vinyl units/nm², indicating less than the theoretical monolayer brush coverage.²⁰

The yields of grafted polymer expressed as milligrams of PVAc/m² of silica are plotted as a function of time in Figure 5. The progress of the homopolymerization and graft polymerization reactions, for the three different initial monomer concentrations, all approximately followed first-order kinetics (see Figures 5 and 6); the least-squares fits to the data also indicated that the graft yields were nearly proportional to their respective initial monomer concentrations. Assuming an equal reactivity of the bonded vinyl groups in the three cases, an increase in PVAc yield would correspond to an increase average degree of polymerization for the grafted chains. This trend is consistent with the study of Ito³⁴ who documented a degree of polymerization proportional to initial monomer concentration for homopolymerization of vinyl acetate in ethyl acetate.

The results for PVAc adsorption (at the adsorption plateau), from ethyl acetate onto unmodified and vinylsilylated silica, are shown in Table III. In both cases it can be seen that the maximum adsorption value was significantly less than even the

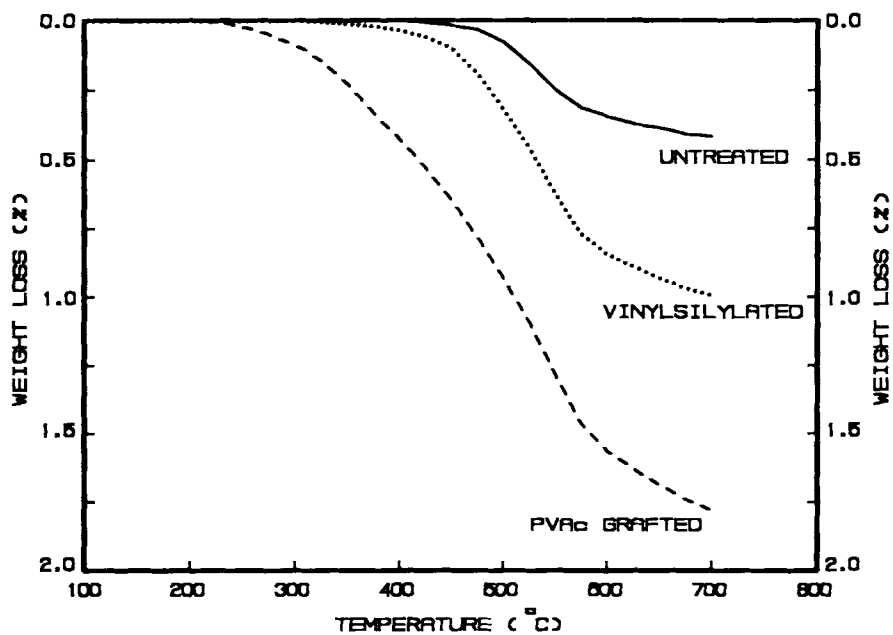


Figure 4 TGA of silicas.

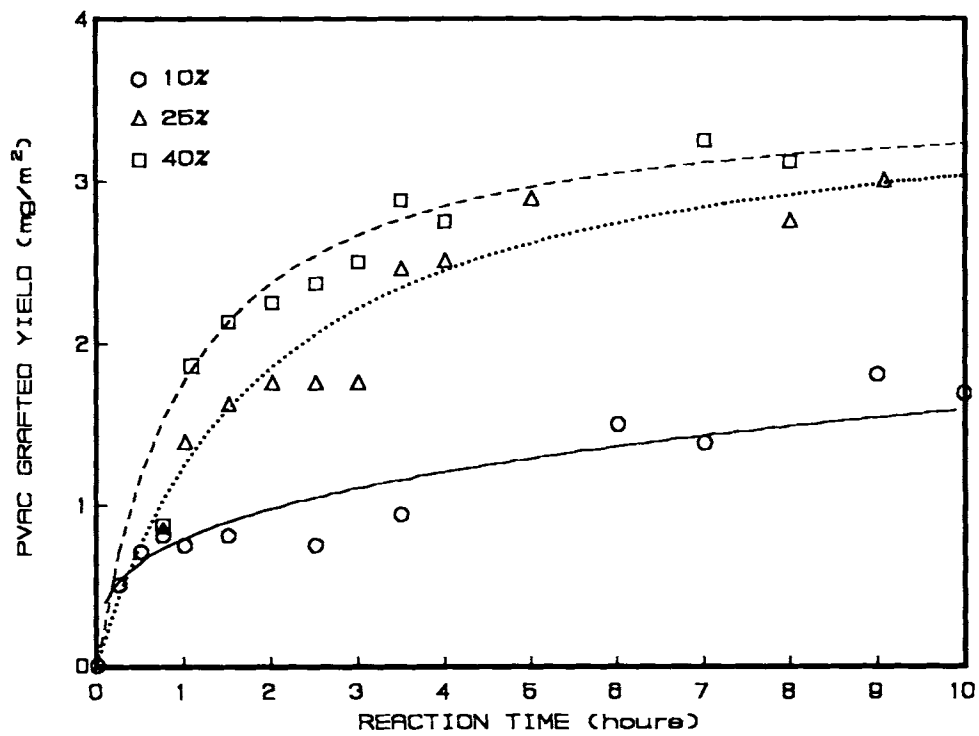


Figure 5 PVAc graft yield at 60°C.

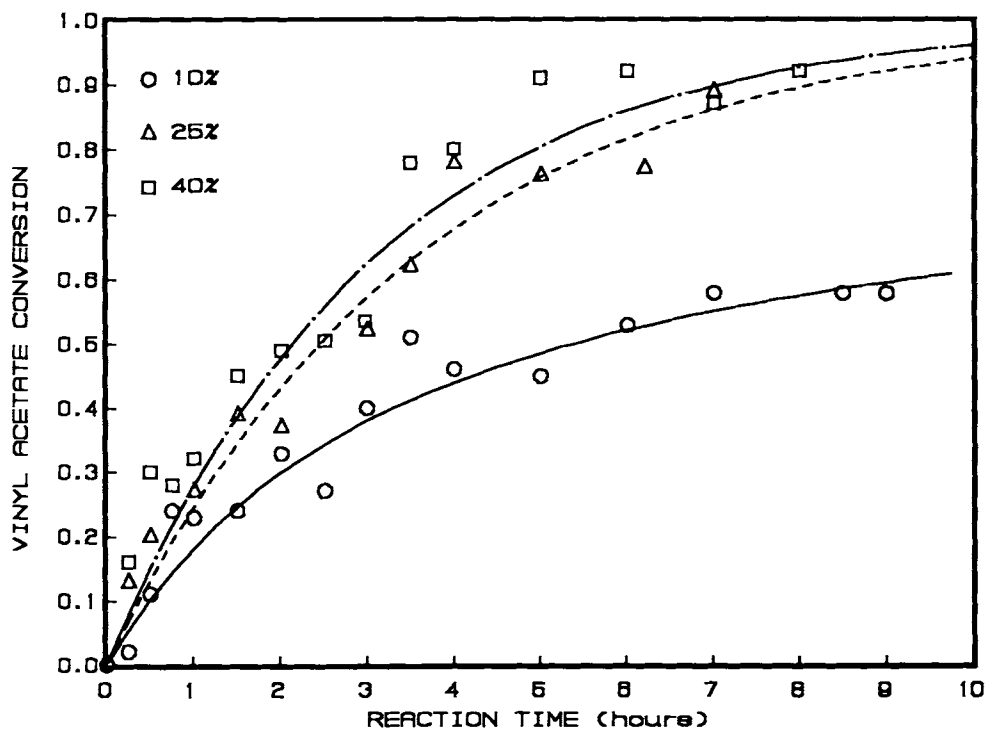


Figure 6 Conversion of VAc monomer at 60°C.

Table II Surface Coverage by Vinyl(triethoxy)Silane and PVAc

Initial Monomer Concentration (v/v)	Vinylsilane Surface Coverage ($\mu\text{mol}/\text{m}^2$)	Highest Polymer Graft Yield (mg/m^2)
10%	39	1.7
25%	32	2.8
40%	40	3.2

Table III Plateau Adsorption Values for Polyvinylacetate

Molecular Weight	Vinylsilane Modified (mg/m^2)	Unmodified (mg/m^2)
90,000	ND ^a	ND ^a
500,000	0.31	0.26

^a The adsorption level was below the detection limit ($\leq 0.001 \text{ mg}/\text{m}^2$).

lowest amount of grafted PVAc achieved. Hence, it was unlikely that any of the given homopolymer adsorbed during the grafting reaction. Given the various washing steps, it is concluded that the reported polymer graft yields are free from any potential errors due to polymer adsorption.

CONCLUSIONS

A method for the free-radical graft polymerization of PVAc onto nonporous silica was described. The grafting procedure is based on an adaptation of the procedure of Chaimberg et al.¹² for graft polymerization of vinylpyrrolidone. With the present silylation procedure, a multilayer vinylsilane coverage of 23–26 vinyl groups/ nm^2 (32–40 $\mu\text{mol}/\text{m}^2$) was achieved. Grafted polymer yields, at 60°C, were roughly proportional to the initial monomer concentration, and the overall rate of grafting followed first-order kinetics with respect to monomer concentration. Conversion of the monomer, vinyl acetate, also followed first-order kinetics at 60°C. Homopolymer adsorption studies in ethyl acetate revealed that a negligible amount of polymer adsorbed onto the vinyl-modified silica. Thus, in the present graft polymerization method, any homopolymer produced during the course of the grafting reaction would not adsorb appreciably onto the vinyl-modified silica particles in the mixture.

Studies are currently underway to evaluate the utility of PVAc-grafted silica resins for the selective removal of organics from aqueous systems and the reverse-phase liquid chromatography of chlorinated hydrocarbons.

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