Graft Polymerization of Polyvinylpyrrolidone onto Silica

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Synopsis

A new technique is reported for the surface grafting of polyvinylpyrrolidone (PVP) to hydroxylated solid surfaces. Free radical graft polymerization of vinylpyrrolidone onto vinylsilane–modified impermeable silica particles was carried out in an aqueous slurry reactor. The graft yield and the monomer conversion were determined by thermogravimetric analysis and UV spectroscopy, respectively. The graft yield was shown to increase by increasing the initial monomer concentration. A comparison of the graft polymerization reaction with the adsorption of polyvinylpyrrolidone onto untreated, vinylsilane-modified, and PVP-grafted silica was performed.

INTRODUCTION

Surface modification by grafting polymer chains to solid substrates is a useful method for the creation of materials which possess specific surface and structural properties. In particular, surface-grafted water-soluble polymers, which are of interest in this work, have been investigated for use as chromatographic support resins[1,2] and biocompatible hydrogels.[3-5] For example, the attachment of polymeric chains to solid surfaces changes the interfacial properties of the substrate, and thus provides a method of controlling the interactions between surfaces and solutes (i.e., adsorption of proteins onto hydrogels or HPLC resins).

Polymer chains may be grafted to the surface of a solid by either graft polymerization or polymer grafting. Graft polymerization involves the growth of polymer chains from the surface active sites by a step or chain polymerization reaction mechanism, while polymer grafting involves the chemical bonding of live polymer chains to the support surface. Polymer grafting allows for the attachment of monodisperse polymers while virtually eliminating bulk homopolymerization. However, since polymer molecules must diffuse to the solid surface, diffusional limitations and steric hindrance effects severely reduce the degree of surface coverage and graft yield obtained by the technique of polymer grafting.[6] In contrast, in graft polymerization diffusion limitations and steric hindrance effects in both porous and nonporous supports are diminished due to the smaller size of the monomer molecules. Thus, a higher surface concentration and a more uniform surface coverage (especially for porous supports) by a grafted polymer layer are possible.

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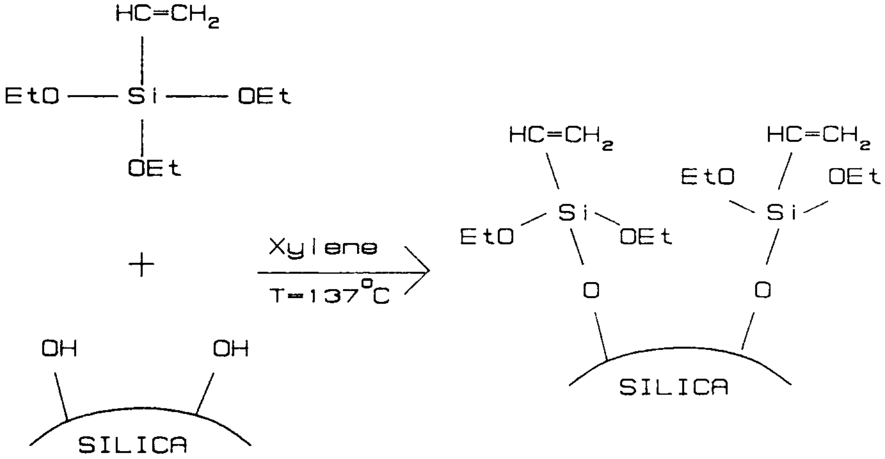

Fig. 1. Organic silylation of vinyltriethoxysilane onto silica.

Graft polymerization can be accomplished provided that surface active sites are available for reaction with a monomer. For example, typical silica substrates, with a surface hydroxyl concentration of approximately[7] 4.6/nm^2 often require chemical modification of the surface hydroxyl groups in order to create surface active sites. Surface active sites on the silica surface can be produced by the formation of siloxane bridges[8-10] as well as by the utilization of surface coupling agents.[11-15]

Organosilanes are used extensively as coupling agents with the oxides of silica, aluminum, zirconium, titanium, and nickel[16] and modifiers of interfacial properties.[16-21] A particularly effective class of silane coupling agents are those of the form $RSiX_3$, where X is a hydrolyzable group (i.e., halogen, amine, alkoxy, acyloxy) and R is a nonhydrolyzable organic group. The desired characteristics of the silane are determined by the choice of the functionality of the R group. For example, vinylsilanes, in which the R is a vinyl group, provide the necessary vinyl surface active sites for graft polymerization.[11-15] Surface-bonded vinyl groups can be formed by organic silylation reactions as shown in Figure 1. The surface-bonded vinyl groups can react with various vinyl monomers through a free-radical polymerization reaction scheme to form surface-grafted polymers.

This study demonstrates the graft polymerization of a water-soluble polymer onto hydroxylated silica surface. The model system explored in this study is the free-radical graft polymerization of vinylpyrrolidone onto silane-modified impermeable silica particles. The above model system should be of interest in a number of biomedical applications since polyvinylpyrrolidone is a nontoxic and biocompatible polymer.

EXPERIMENTAL

Graft polymerization of vinylpyrrolidone onto impermeable modified silica particles was studied in an aqueous slurry batch reactor. The graft polymerization procedure consisted of a surface modification with vinyltriethoxysilane followed by the surface polymerization of vinylpyrrolidone which resulted in a chemically bonded polyvinylpyrrolidone phase. The graft yield was determined by thermogravimetric analysis. In addition, UV spectral analysis was used to determine the conversion of monomer into polymer, and HPLC analysis was utilized in the determination of the homopolymer molecular weight.

Materials

Nonporous silica particles (Novacite L207-A), with an average diameter of 5.0 μm, were supplied by Malvern Minerals Co. (Hot Springs, AR). The surface area was determined by BET nitrogen adsorption to be approximately 2.0 m^2/g. Vinylpyrrolidone (1-vinyl-2-pyrrolidinone) monomer, with 0.1% potassium hydroxide as inhibitor, was supplied by Kodak Chemical Co. (Rochester, NY). Surface silylation was carried out with vinyltriethoxysilane obtained from Petrarch Systems Inc. (Bristol, PA). Reagent-grade xylene was used in the silylation reaction. A 58% aqueous solution of ammonium hydroxide (Mallinckrodt Inc., Paris, KY) was the source of ammonium ions used in the graft polymerization. The initiator was reagent-grade hydrogen peroxide available as a 30% solution (Aldrich Chemical Co., Milwaukee, WI). Finally, PVP fractions with number average molecular weights of 10,000 and 360,000 (Aldrich Chemical Co.) were used for the physical adsorption studies.

Silylation

Prior to silylation, the silica particles were washed with dilute hydrochloric acid and dried at 150°C under vacuum to remove surface water.[22] The organic silylation reaction was performed in a reflux condenser, for 5 h, using a 10% solution of vinyltriethoxysilane in xylene[21] (see Fig. 2). The condenser was kept at a temperature above the boiling point of the displaced alcohol (in this case ethanol) but below the boiling point of the silane solution. The particles were then washed several times with xylene and allowed to cure overnight at 50°C under vacuum.[23] In order to hydrolyze the remaining ethoxy groups, the silylated silica particles were kept dispersed in water at a pH of 9.5 for 3 days.[24] During the hydrolysis step the silica particles changed from displaying hydrophobic behavior to hydrophilic behavior as expected due to the replacement of ethoxy groups by hydroxyl groups (Fig. 3).

The amount of surface-bonded vinylsilane was determined by thermogravimetric analysis (TGS-2, Perkin-Elmer, Norwalk, CT) of the silylated silica particles. Initially, the sample particles were heated to 100°C and held at that temperature until no weight loss was observed over a period of 10 min. This procedure was performed in order to eliminate all nonchemically bonded water. The thermogravimetric analysis consisted of measuring the weight loss upon heating the silica particles in an air atmosphere at 25°C/min from 100 to 700°C. The upper limit of 700°C was sufficient to remove the bonded silane from the silica surface. The amount of surface-bonded vinylsilane was determined by subtracting the weight loss of the virgin silica from the weight loss of the silylated silica sample.

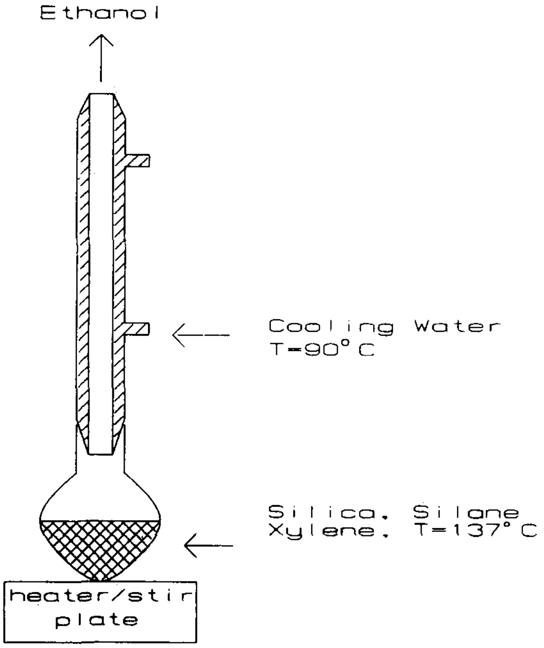

Fig. 2. Silylation reaction apparatus.

Graft Polymerization

The graft polymerization reaction was performed in a 1 L jacketed reaction flask under a nitrogen atmosphere (Fig. 4). All the experiments were conducted at a temperature of 70°C. A nitrogen atmosphere was necessary in order to eliminate atmospheric oxygen which is known to lead to an increase in the latent period of polymerization as well as a reduction in the rate of polymerization.[25] The polymerization procedure consisted of first placing a predetermined amount of silylated silica particles (about 4 g) into the reaction vessel along with a 200 mL solution of vinylpyrrolidone monomer and deionized water. The reaction mixture was slowly heated until the solution reached the desired reaction temperature. The grafting reaction was then initiated with 1.0 mL of hydrogen peroxide (30%) and 0.4 mL of ammonium hydroxide (58%). Ammonium hydroxide acts as a buffer for the reaction mixture and

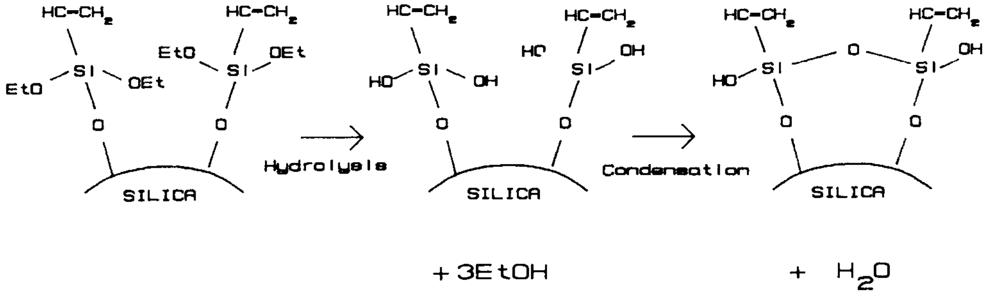

Fig. 3. Silane hydrolysis and condensation.

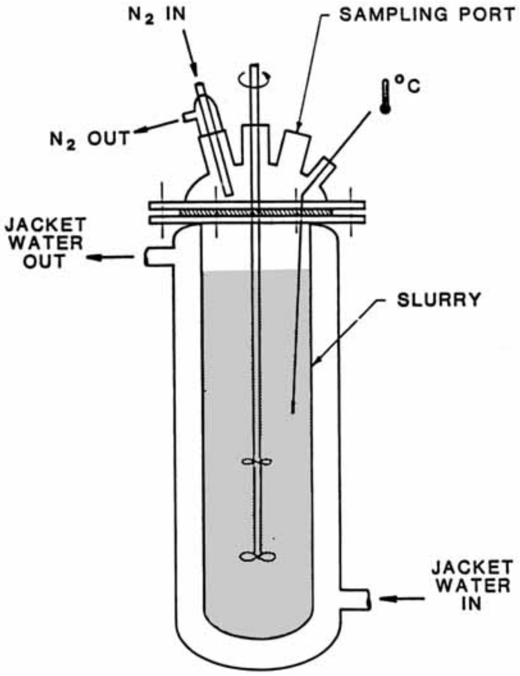

Fig. 4. Graft polymerization reaction apparatus.

thus prevents the formation of the undesirable acetaldehyde by-product under acidic conditions.[25] In addition, ammonium hydroxide has a strong activating effect on the polymerization reaction, shortening the latent period and increasing the rate of reaction.

The reaction mixture was sampled at different times by drawing 2-mL aliquots of the slurry from the reaction vessel. Each sample was filtered with a polyester filter membrane to separate the particles which were subsequently washed thoroughly with room temperature deionized water to remove the free monomer, homopolymer, and polymer not strongly bonded to the silica surface (i.e., weakly adsorbed or entangled polymer). At the end of each experiment the remaining silica was filtered and washed thoroughly with water. All of the silica samples were dried in air at room temperature prior to analysis.

The amount of grafted polyvinylpyrrolidone was determined by thermogravimetric analysis as described above. The conversion of monomer in the reaction mixture was determined by UV analysis (HP 8452A Diode Array Spectrophotometer, Hewlett-Packard, Palo Alto, CA) of the reaction solution. Vinylpyrrolidone monomer and polyvinylpyrrolidone both contain carbonyl groups which absorb UV radiation at 196 nm. However, vinyl groups, which absorb UV radiation at 233 nm, are only present on the vinylpyrrolidone monomer. Therefore, by taking the ratio of the absorbance at 233 and 196 nm, one obtains the ratio of monomer to polymer and the conversion is given as

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

where [monomer] = Abs(233 nm)/Abs(196 nm). In this procedure the carbonyl group is utilized as an internal standard. The concentration of grafted polymer in the reaction mixture was negligible compared to the amount of homopolymer, and, thus, the correction needed to account for the grafted polymer was negligibly small. The molecular weight of the homopolymer was determined using HPLC size exclusion chromatography (Varian 5000, Downey, CA).

Finally, in order to assess the possibility of physical adsorption of the homopolymer from the aqueous reaction mixture onto the silylated and PVP-grafted silica particles, evaluative adsorption experiments with PVP fractions of number average molecular weights 10,000 and 360,000 were carried out. PVP adsorption onto the silylated and PVP-grafted particles was carried out over an equilibration period of 1 week at a temperature of 23°C. The amount of adsorbed PVP was determined by measuring the initial and final solution concentrations using both a refractive index monitor (Model 1750, Bio-rad, Cambridge, MA) and UV analysis.

RESULTS AND DISCUSSION

The surface silylation results obtained by thermogravimetric analysis indicate a surface concentration of approximately 9.0 vinyl units/nm^2. For an initial surface hydroxyl concentration of approximately 4.6/nm^2, the silylation reaction resulted in the bonding of approximately two vinylsilane groups for each available surface hydroxyl group. This high degree of surface coverage is indicative of a multilayer coverage of vinylsilane chains on the silica surface. In contrast, previous attempts at silylation using the aqueous technique[16] resulted in surface vinyl concentration of less than 1.0 vinyl units/nm^2 and thus incomplete surface coverage. The stability of the silylated silica particles was evaluated by exposing the silica particles to water at a pH of 7.0 for up to 10 days with the results of no apparent decrease in the surface vinyl concentration. This result is consistent with the results of Chang et al.,[20] who previously demonstrated the hydrolytic stability of $Si-O-Si-C$ bonded phases for silane-bonded silica. Although it is difficult to draw definitive conclusions from the above studies regarding the stability of the silane layer during the graft polymerization reaction, the high polymer graft yield obtained (Fig. 5) supports the contention that the bonded silane remained intact.

The graft yield, defined as the mass (mg) of grafted polymer per square meter of silylated silica, as a function of reaction time is shown in Figure 5. For initial monomer concentrations of 50, 30, and 10%, the highest graft yields obtained were approximately 2.5, 1.3, and 1.1 mg PVP/m^2, respectively, and the lower limit of the number average molecular weights were estimated to be 1500, 780, and 660, respectively. The average molecular weight of the grafted polymer was estimated by assuming that each of the surface vinyl groups resulted in a grafted polymer chain. The corresponding molecular weights of the homopolymer (M_n and M_w) are given in Table 1. For each of the experiments, carried out at initial vinylpyrrolidone monomer concentrations of 30 and 10%, the graft polymerization reaction followed approximately first-order kinetics with respect to the monomer concentration throughout the

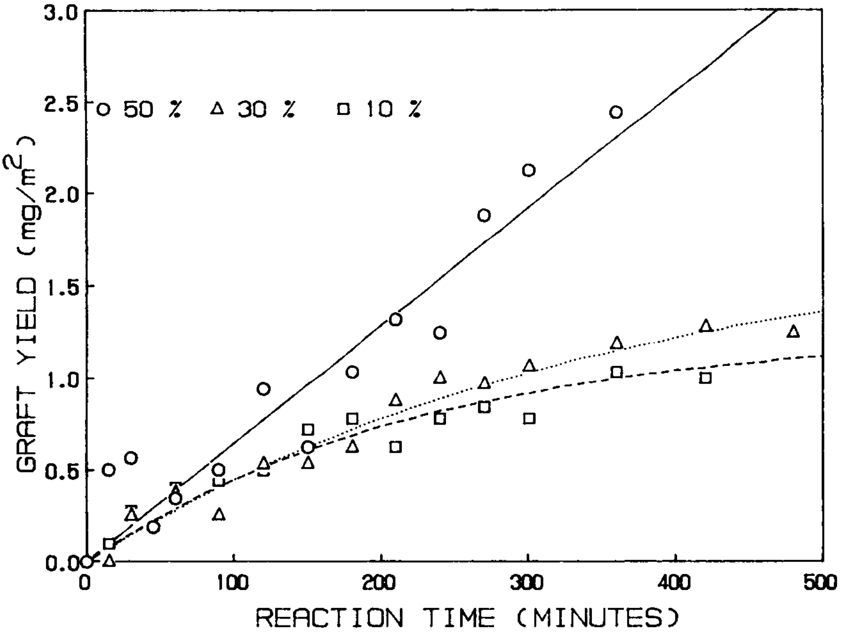

Fig. 5. Graft yield of PVP onto silica: (○) 50%; (△) 30%; (□) 10%.

reaction. It appears, however, that for an initial monomer concentration of 50%, the order of the reaction, with respect to monomer concentration, was much less than unity. In order to understand the above behavior, it is useful to compare the graft polymerization results (Fig. 5) with the results for the monomer conversion in the bulk solution.

The conversion of monomer to homopolymer was determined from the UV absorbance spectrum of the reaction solution at various times during the reaction, as illustrated in the typical spectra of Fig. 6. It is evident that, as the reaction proceeds, the absorbance due to the vinyl groups decreases with respect to the absorbance corresponding to the carbonyl groups. The decrease in the absorbance due to the vinyl groups is an indication that the vinylpyrrolidone is reacting to form polymer. The initial rates of both homopolymer and graft polymer formation increase with increasing monomer concentration (Figs. 5 and 7). These homopolymerization results are qualitatively equivalent to previous homopolymerization studies which demonstrated an increase in the initial rate of polymerization with an increase in the vinylpyrrolidone concentration.[25] For each of the initial monomer concentrations studied, however, while the conversion approached a value of approximately 80% after about eight hours, the final graft yield was independent of the conversion of homopolymer.

A comparison of the graft yield with the monomer conversion indicates that the amount of grafted polymer is correlated with the initial rate of homopolymerization. Although the rate of monomer conversion decreases significantly during the reaction, the rate of graft polymerization decreases to a lesser extent (especially as the initial monomer concentration increases) over the same time period. At low conversion, graft polymerization dominates the grafting reaction, and the rate of grafting is proportional to the monomer

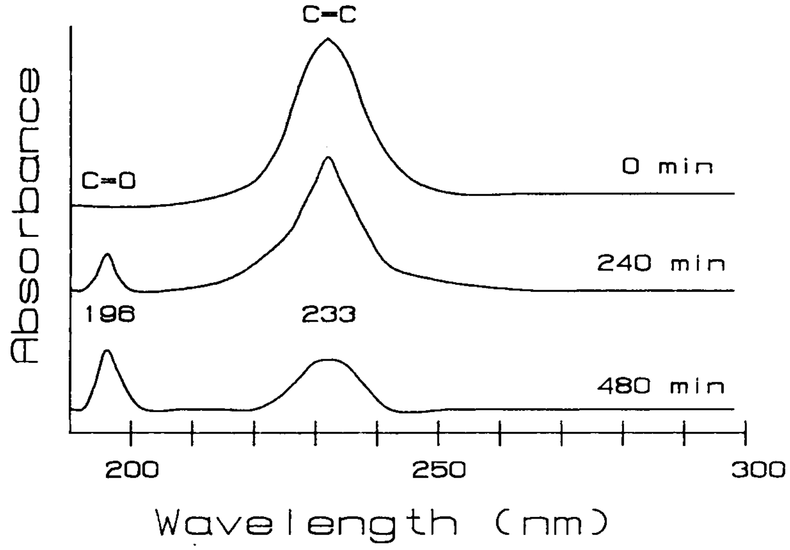

Fig. 6. UV absorption spectra of reaction solution.

concentration. At high conversion, living homopolymer chains may graft onto the substrate, thereby leading to the lower dependence of the rate of grafting on the monomer concentration. This behavior is especially evident for the 50% initial monomer concentration experiment, where the high rate of homopolymerization leads to a high concentration of live polymer chains that may graft directly onto available surface sites. A detailed discussion of the above kinetic

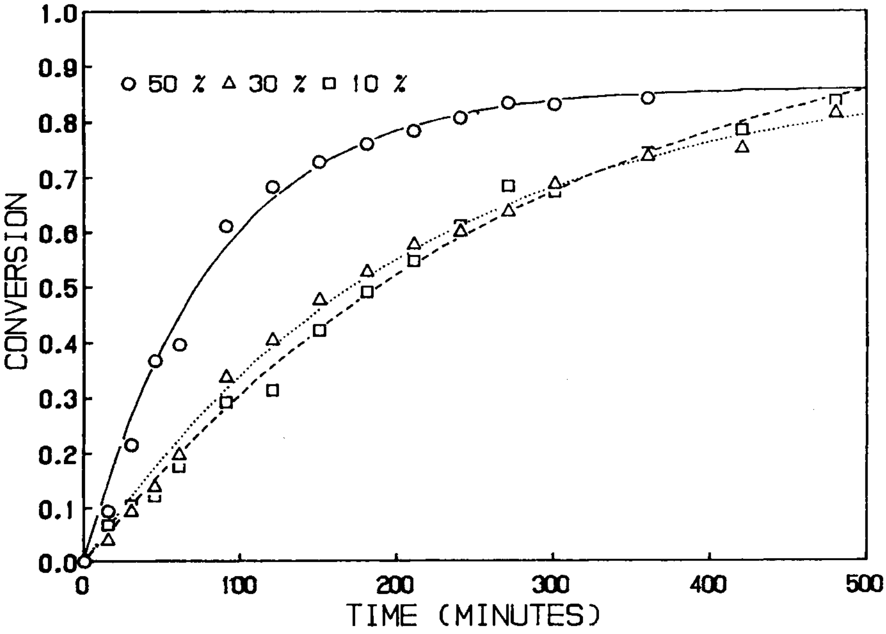

Fig. 7. Conversion of vinylpyrrolidone: (○) 50%; (△) 30%; (□) 10%.

TABLE I
Molecular Weights of Homopolymer

Initial monomer concentration	M_n	M_w	M_w/M_n
10%	10,500	14,200	1.3
30%	24,700	34,500	1.4
50%	36,900	51,300	1.4

behavior is beyond the scope of the current paper. A complete study of the dependence of graft polymerization and polymer grafting on the graft yield, as well as a detailed study of the kinetics of graft polymerization of PVP, will be described in a separate publication. Finally, the possibility of homopolymer adsorption onto the silica surface was assessed by conducting a series of adsorption experiments as described previously.

The adsorbance at the adsorption plateau for two fractions of PVP (M_n = 10,000 and M_n = 360,000) onto untreated, vinyl-modified and PVP-grafted silica particles are given in Table II.[26] The adsorbance values for the untreated silica (approximately 1.0 mg PVP/m^2) are consistent with the results obtained by other authors for the adsorption of PVP onto silica particles.[27,28] The details of the adsorption study and the discussion of the effect of surface chemistry for a variety of different surfaces on the adsorption of PVP are the subject of a subsequent paper.[29] Here it suffices to note that the amount of PVP that can be adsorbed onto vinyl-modified silica particles is significantly less than the maximum amount of grafted PVP. Moreover, the amount of PVP adsorbed onto PVP-grafted silica is negligible compared to the amount of PVP adsorbed onto either virgin or vinyl-modified silica. The fact that adsorption of PVP onto PVP-grafted silica is virtually eliminated suggests that, once PVP has been grafted onto the surface of the silica particles, there is only a limited amount of PVP (less than 10% of the amount of grafted PVP) that will adsorb onto the PVP-grafted particles. Further support for the above hypothesis is provided in the recent study of Cohen Stuart et al.,[30] which suggests that adsorbed PVP will be displaced from the surface of silica substrates by the vinylpyrrolidone monomer. Hence, it can be concluded that initially adsorbed monomer, as opposed to adsorbed polymer, will be the predominant species on the silica surface. As the grafting reaction proceeds, any adsorbed homopolymer will be displaced by the monomer and/or the growing grafted polymer chains thereby further lowering the amount of homopolymer adsorption (Table II).

TABLE II
Plateau Values of Aqueous PVP Adsorption (mg/m^2)

M_n	Untreated silica	Vinyl-modified silica	PVP-graft silica
10,000	0.8	1.1	0.1
360,000	1.0	1.5	< 0.1

CONCLUSION

This study demonstrated that grafting of hydrophilic polymers by graft polymerization is feasible. The modification of the silica surface through reaction with vinyltriethoxysilane resulted in a surface coverage of approximately 9 vinyl groups/nm^2. Graft polymerization of PVP onto vinyl-modified silica particles followed approximately first-order kinetics with respect to the monomer concentration for initial monomer concentrations of 10 and 30%, and less than first-order kinetics for an initial monomer concentration of 50%. The rate of grafting was shown to increase with an increase in the initial monomer concentration. The lower limit estimate of the average molecular weight of the grafted polymer, based on initiation of each surface vinyl group, was 660, 780, and 1550 for initial monomer concentrations of 10, 30, and 50%, respectively.

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