Permeability of Graft-Polymerized Polyvinylpyrrolidone–Silica Resin in Packed Columns

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The effect of solvent power and flow rate on the permeability of a size exclusion chromatography (SEC) column packed with a novel polyvinylpyrrolidone (PVP)-grafted porous silica resin was studied. The PVP-silica resin was prepared from a porous silica size exclusion resin onto which a terminally anchored PVP layer was graft polymerized. The terminally anchored PVP layer was synthesized via a free radical graft polymerization method. The permeability of the PVP-grafted silica columns was determined from simple flow rate–pressure drop measurements. Qualitatively, as the solvent power increased, the permeability of the PVP-silica-packed column decreased. This behavior was consistent with the expected higher degree of swelling of PVP with increasing solvent power. The permeability was also lower for longer PVP surface-anchored chains. The change in the permeability of the PVP-grafted columns with shear stress was negligible, consistent with the estimate of a dense brush-like surface coverage by terminally anchored PVP molecules. The possibility of controlling the surface conformation of the PVP layer by changing the solvent power and possibly shear rate (for nonbrush coverage) suggests an additional degree of freedom in operating SEC columns. The use of polymer–silica matrix resins in size exclusion chromatography may be of special interest since one can tailor-design the surface by controlling the degrees of surface density and grafted polymer molecular weight. © 1992 Academic Press, Inc.

INTRODUCTION

Surface modification by polymer grafting (1–5) and graft polymerization (3, 6–10) onto silica resins constitute a useful method for the creation of separation resins which possess specific surface and structural properties, and still maintain the high mechanical strength of inorganic gels used in size exclusion chromatography (SEC). For example, the attachment of polymeric chains of specific functionality to silica SEC resins is one method of minimizing surface adsorption in SEC (6, 11–13) and thus minimizing adverse effects such as peak shifts and peak broadening.

Although there are now a number of studies that have focused on the synthesis of terminally anchored polymer layers for SEC applications (12), little attention has been devoted to investigating the swelling of such layers as a function of solvent power or their deformation when subjected to solvent flow in SEC columns. One should expect that a grafted polymer layer would expand in a good solvent and collapse as the solvent quality decreases. In addition, by changing the solvent flow rate, for a given column packing resin and geometry, the grafted polymer layer can deform such that its effective thickness would change due to shear-induced deformation (14–18). Thus, with surface grafted polymer–silica resins one may have the ability to control the physical conformation of the surface polymer layer by both changing the solvent quality and controlling the solvent flow rate.

Recently, Parnas et al. (13) showed that the adsorption of polyvinylpyrrolidone (PVP) graft-polymerized silica surface is virtually eliminated relative to a virgin silica surface. This suggests that a PVP–silica resin could be useful for size exclusion chromatography of PVP and potentially other water-soluble poly-
mers. In this paper we report on the investigation of the swelling of a PVP layer in which the individual PVP chains are terminally anchored onto a silica size exclusion chromatography resin. Specifically, the permeabilities of graft-polymerized PVP-silica-packed columns are reported as a function of the solvent power and solvent pore-wall shear stress. In a future study we will report on the coupling between the grafted layer deformation and the separation performance of such modified resins in polymer SEC applications.

EXPERIMENTAL

Materials

Porous silica particles (Nucleosil 1000-10) were supplied by the Rainin Company (Woburn, MA). The average particle diameter was determined to be 8.6 μm from images using scanning electron microscopy (SEM). The surface area, pore size, and pore volume of the silica particles, as reported in Table I, were determined using a nitrogen adsorption system (Autosorb-1, Quantachrome Corporation, Syosset, NY).

Vinyltriethoxysilane used for surface silylation was obtained from Petrarch Systems Inc. (Bristol, PA). Reagent-grade xylene and potassium hydroxide (Fisher Scientific, Pittsburgh, PA) were used as solvent and hydrolyzing agent, respectively, in the silylation reaction. Vinylpyrrolidone (1-vinyl-2-pyrroldone; 98%) containing 0.1% potassium hydroxide as inhibitor, supplied by Kodak Chemical Company (Rochester, NY), was used as the monomer for the graft polymerization reaction. A 58% aqueous solution of ammonium hydroxide (Mallinckrodt Inc, Paris, KY) was used as a source of ammonium ions and reagent-grade hydrogen peroxide available as 30% solution (Aldrich Chemical Co, Milwaukee, Wisconsin) was used as initiator (19).

The mobile phases used in the pressure drop–flow rate experiments were deionized, filtered (0.2-μm filter) water; water:acetone mixture (33.2:66.8 v/v), which is a theta solvent for PVP at 25°C; and aqueous sodium sulfate solution (0.55 M; J. T. Baker Chemical Co., Phillipsburg, NJ), which is a theta solvent for PVP at 28°C.

Graft Polymerization

Two distinct PVP-grafted silica resins (see Table III) were prepared by the free radical graft polymerization method of Chaimberg et al. (19) and Cohen and Chaimberg (20). Resins G1 and G2 were prepared using a porous silica resin (Nucleosil 1000-10) onto which PVP was graft polymerized starting with different initial monomer concentration.

The graft polymerization procedure consisted of first silylating the silica particles with vinyltriethoxysilane using xylene as the solvent. The resulting surface-bound silane groups (Fig. 1) were subsequently hydrolyzed in a basic aqueous solution (19–22) to convert the silylated silica surface to a hydrophilic form through replacement of the ethoxy groups with hydroxyl groups. Subsequently, the PVP-grafted silica was prepared by a free radical graft polymerization reaction in which vinylpyrrolidone was used as the monomer. The polymerization reaction was carried out in an

<table>
<thead>
<tr>
<th>Silica type</th>
<th>Average particle diameter (μm)</th>
<th>Average BET surface area (m²/g)</th>
<th>Average pore diameter (Å)</th>
<th>Total pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucleosil 1000-10</td>
<td>8.6</td>
<td>22.2</td>
<td>1200</td>
<td>0.616</td>
</tr>
</tbody>
</table>

TABLE I
Properties of Unmodified Silica Supports

aqueous medium in a slurry reactor at 70°C resulting in a terminally anchored PVP layer as well as homopolymer (Fig. 2). The vinylsilane concentration and the polymer graft yield were determined by thermogravimetric analysis (TGS-2, Perkin-Elmer, Norwalk, CT). 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 thermally degrade, combust, and volatilize the bonded silane and grafted polymer off the silica surface (19).

Flow Experiments

The flow rate–pressure drop behavior was determined for a number of different solvents flowing through stainless-steel columns (25-cm length, 0.46-cm i.d., with 2-μm frits; Beckman Instruments, Fullerton, CA) packed with the unmodified and polymer–silica resins. Packed columns were fitted inside a water jacket through which water was fed from a constant-temperature reservoir to maintain constant temperature for the columns during the experiments. The columns were packed by the slurry technique using an Isco pump Model 3250 (Isco Inc., Lincoln, NE).

The pressure drop–flow rate measurements were performed using an HPLC pump (Isco Model 3250). A gradient programmer (Isco Model 2360) was employed when a solvent mixture was used as the mobile phase. Flow

<table>
<thead>
<tr>
<th>Mobile phase</th>
<th>Viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water at 25°C</td>
<td>0.890</td>
</tr>
<tr>
<td>Water:acetonitrile (33.2:66.8 v/v) at 25°C (theta solvent for PVP)</td>
<td>1.023</td>
</tr>
<tr>
<td>Water at 28°C</td>
<td>0.833</td>
</tr>
<tr>
<td>Sodium sulfate (0.55 M) at 28°C (theta solvent for PVP)</td>
<td>1.046</td>
</tr>
</tbody>
</table>
curves were determined by starting at the lowest flow rate and tracing back from the high flow rate back to the lowest flow rate to check the reproducibility of the data. The viscosities of the mobile phases were measured with Cannon–Fenske viscometers (Cannon Instruments Co., State College, PA) temperature controlled using a constant-temperature bath. The viscosities of the different mobile phases are given in Table II.

RESULTS

The vinyl group concentration and polymer graft yield are reported in Table III. The vinylsilane surface concentration was the same for both resins G1 and G2. However, the resulting polymer graft yield (mg polymer/m²) was about 70% higher for resin G1 relative to resin G2; thus, it is likely that the grafted polymer chains were longer for resin G1. Since the resins were porous it was not feasible to determine the molecular weight of the graft-polymerized layer in the porous resins by conventional analytical methods. Recently, however, Chaimberg (21) and Chaimberg and Cohen (22) provided a detailed analysis of the molecular weight of graft-polymerized PVP for various reaction conditions. Based on their results and the reaction conditions employed in this study we estimate that the number-average molecular weights for the PVP layer for resins G1 and G2 were approximately 13,500 and 7000, respectively. It is important to note that the grafting efficiency for graft polymerization is low (i.e., only a small fraction of the surface vinyl sites react). The results of the present study suggest that the fractions of surface vinyl groups which react to form grafted polymer chains was 0.059 and 0.068 for resins G1 and G2, respectively. The corresponding surface densities of the terminally graft-polymerized PVP were about 0.13 and 0.15 μmole/m² for resins G1 and G2, respectively.

As grafted chains are crowded on the silica surface the polymeric coils will begin to overlap. According to the simple scaling analysis presented by de Gennes (23) chain overlap will occur when the following condition is obeyed:

\[(a/D)^2 > N^{-6/5}\]

Here, \(D\) is the average distance between grafted sites, \(a\) is the monomer size, and \(N\) is the number of monomers per grafted chain. Given the polymer graft yield, the estimated molecular weight of the grafted layer, and the approximate diameter of the chain (about 8 Å), the average distance between grafted sites on the surface, for both resins, is about 40 Å and the numbers of monomers per chain are about 121 and 63 for resins G1 and G2, respectively. Thus, it can be easily verified that the above inequality is satisfied and thus the terminally grafted PVP layer is of the dense "brush-type" layer and thus for a good solvent it will be in the stretched chains (23). Our estimate of the effective diameter of the chain is a lower estimate since it is based on a stretched chain. It is expected that if the diameter of chain "blobs," as defined by de Gennes (23), is used then a higher effective chain diameter will result and thus Eq. [1] will still hold. Given that the grafted polymer chains are in a "dense" brush-like conformation, solvent flow through the polymer surface layer would be hindered.

The stretching of the polymer layer is determined by a balance between the osmotic swelling of the dense brush and the restoring elastic forces that resist swelling. Thus, one would expect that the grafted polymer layer will swell to different degrees depending on the solvent power. An indirect indication of the swelling of the terminally anchored poly-

<table>
<thead>
<tr>
<th>Type of column</th>
<th>Silica type</th>
<th>Vinyl group concentration (μmole/m²)</th>
<th>Polymer graft yield (mg/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1 (30% VP)*</td>
<td>Nucleosil 1000-10 (Batch 8121)</td>
<td>2.22</td>
<td>1.79</td>
</tr>
<tr>
<td>G2 (10% VP)</td>
<td>Nucleosil 1000-10 (Batch 8121)</td>
<td>2.22</td>
<td>1.05</td>
</tr>
</tbody>
</table>

* VP, vinylpyrrolidone.

The permeability of a packed column can be determined from simple flow rate–pressure drop measurements using Darcy’s law

\[ Q = k \frac{A \Delta P}{\mu L} \]  

where \( Q \) is the flow rate (cm\(^3\)/s), \( A \) is the cross-sectional area of the column (cm\(^2\)), \( \Delta P \) is the pressure drop (g cm/s\(^2\)), \( \mu \) denotes the viscosity of the mobile phase (g/cm s), \( L \) is the length of the column (cm), and \( k \) is the permeability (cm\(^2\)). The flow curve for the unmodified silica resin (Fig. 3) was expressed such that the slope is directly equal to the permeability. Based on the results of Fig. 3 and Eq. [2], the permeability of the column, packed with the unmodified resin, was determined to be 7.37 \( \times \) 10\(^{-11} \) cm\(^2\) (independent of the solvent). For columns packed with spherical particles the permeability can be estimated from the relationship

\[ k = \left[ \frac{D_p^2 \epsilon^3}{180(1 - \epsilon)^2} \right] \]  

from which the external porosity, corresponding to the permeability of the unmodified column, was determined to be 0.22.

The flow rate–pressure drop curves for the two different columns (G1 and G2) are shown in Figs. 4 and 5. The significant differences in the flow rates, for a given pressure drop, for the different solvents are larger than can be attributed to the difference in the solvent viscosities (Table II). For example, at a column pressure of 2.07 \( \times \) 10\(^7\) Pa, the flow rate of the water:acetone mixture through column G1 (25°C) is about 56% higher than for pure water, while the viscosity difference indicates a flow rate difference of only 12%. Such behavior may be attributed to the graft-polymerized PVP layer and its interaction with the solvent. In water, which is a better solvent for PVP relative to the water:acetone (33.2:66.8 v/v) mixture, the PVP layer is expected to be more stretched (or swelled) and offer greater hydrodynamic resistance to solvent flow and thus affect the permeability of the column to the given solvent. Although it was not possible to determine the actual thickness of the surface polymer layer, the permeability of the column can serve as a qualitative indication of the degree of swelling of the surface polymer layer. In reality, the flow field in the packed columns is complex given that both shear and elongational components may affect the conformation of the surface polymer layer. Qualitatively, a decrease in the permeability would correspond to an increase in the thickness of the surface layer.

The permeabilities for the packed columns, for the different solvents (Table II), were calculated from Eq. [2] and expressed as a function of the pore-wall shear stress (24) defined as

\[ \tau = \frac{A \Delta P}{(L_e/L)(L/R_h)} \]  

where the hydraulic radius \( R_h \) is given by

\[ R_h = \left[ \frac{D_p \epsilon}{6(1 - \epsilon)} \right] \]  

where \( D_p \) is the particle diameter (cm\(^2\)), \( \epsilon \) is the porosity of the unmodified packed column, and \( L_e/L \) is the ratio of the effective fluid path length to the length of the column. For spherical packing the value of \( L_e/L \) can be taken to be 1.57 (24). The permeabilities of the col-

![Fig. 3. Flow curve for the unmodified Nucleosil 1000-10 resin using different solvents.](image-url)
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Columns packed with resins G1 and G2 are shown in Figs. 6 and 7, respectively. These results demonstrate higher permeabilities for resin G2 than for resin G1. This behavior is consistent with the assertion of longer grafted PVP chains for resin G1 relative to resin G2. Also consistent with the above observation is the greater expansion of the grafted polymer, for resin G1 relative to resin G2, in water (good solvent) relative to the theta conditions, at the same temperature. Figures 6 and 7 clearly illustrate that the permeability is lower in a good solvent compared with the theta solvent condition. This result is not surprising given that greater repulsion among segments of the polymer chains is expected with increasing solvent power.

It is interesting to note that the permeability of the PVP–silica resin to water flow increased with increasing temperature. This behavior is consistent with fact that the solvent power of water for PVP decreases with increasing temperature (25), resulting in a lower swelling of the PVP surface layer with increasing temperature. Another interesting observation is that the permeability of the PVP–silica-packed columns was lower for water:acetone (33.2:66.8 v/v) at 25°C than for the aqueous sodium sulfate 0.55 M solution at 28°C, even though both are theta solvents for PVP (26). The difference in permeability between the above two theta solvents is consistent with the estimates of the unperturbed end-to-end distance of PVP in these solvents. Meza and Gargallo (26) cor-

related the intrinsic viscosity for PVP using the Stockmayer–Fixman equation (27):

\[
[\eta]M^{-1/2} = K_\theta + 0.51\phi_0 BM^{1/2} \quad [6]
\]

and

\[
K_\theta = [\eta_0]/M^{1/2} = \phi_0(\langle r_0^2 \rangle/M)^{3/2} \quad [7]
\]

where \([\eta]\) is the intrinsic viscosity, \(M\) is the molecular weight, \(B\) is the second virial coefficient, \(\langle r_0^2 \rangle^{1/2}\) is the root mean square (rms) unperturbed end-to-end distance for the chain, and \(\phi_0\) is a universal constant. Meza and Gargallo (26) determined the values of \(K_\theta\) to be \(74 \times 10^{-5}\) and \(58 \times 10^{-5}\) for water:acetone (33.2:66.8 v/v) at 25°C and for sodium sulfate 0.55 M at 28°C, respectively. Thus, from Eq. [7] it can be inferred that the rms end-to-end distance \(\langle r_0^2 \rangle^{1/2}\) for PVP chains in solution, in water:acetone (33.2:66.8 v/v) at 25°C, is larger by 8.5% than the \(\langle r_0^2 \rangle^{1/2}\) value for PVP in 0.55 M sodium sulfate at 28°C. The corresponding difference in permeability at high shear stress between the two theta solvents is about 28% (at stress levels above about 0.03 Pa), which suggests that the permeability is a sensitive function of the thickness of the polymer surface layer.

The variation of the permeability with the pore-wall shear stress as indicated in Figs. 6 and 7 reveals that the G1 resin for which the molecular weight of the grafted layer was higher did not display a significant variation of the permeability with shear rate. This behavior is indicative of a dense PVP surface layer that does not deform with shear rate, or it may have already reached the minimum layer thickness, as commonly observed for adsorbed layers (16–18), at the lowest shear stress levels employed in this study. For the lower-molecular-weight PVP–silica resin (G2), the permeability decreased slightly (corresponding to increasing polymer layer thickness) with increasing stress level for water:acetone and for the sodium sulfate solution at a shear stress level below about 200 dyn/cm². It is interesting to note that both for the sodium sulfate solution mobile phase and for water at 28°C an increase in permeability (corresponding to a decreasing polymer layer thickness) was observed at shear stress levels greater than about 250 dyn/cm². This latter behavior resembles the observed variations in the effective hydrodynamic thickness of adsorbed polymers with shear rate and solvent power (16–18).

**CONCLUSIONS**

This study demonstrates that terminally anchored polymer surface layers, prepared by graft polymerization, can significantly affect the permeability of packed liquid chromatographic columns. The permeability measurements suggest that the terminally grafted PVP layer swells with increasing solvent power. The deformation of the grafted polymer layer is also slightly affected by the pore-wall shear stress (or shear rate) although it is recognized that a more significant dependence on solvent

![Fig. 6. Permeability of column G1. Effect of solvent power and pore-wall shear stress.](image)

![Fig. 7. Permeability of column G2. Effect of solvent power and pore-wall shear stress.](image)
flow rate may be observable at shear stress levels lower than obtained in the current study. It is worth noting that based on available theoretical studies it is expected that the conformation of the PVP surface layer will be a function of the PVP surface density. The variation of surface density is difficult to control experimentally and it remains a challenge for future work in this area.

The current work suggests that it may be useful to explore the possibility of using size exclusion resins which are based on a polymer–silica-grafted resin where the conformation of the polymer layer can be adjusted by changing the solvent power. This may provide an additional degree of freedom in operating size exclusion chromatography columns. The utility of polymer-grafted silica resins for size exclusion chromatography will be reported in future work.

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