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Characterization of the pore-surface gel phase in functionalized macroporous polymeric materials

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Abstract Covalently immobilized pore-surface gel phases were prepared in a functionalized macroporous ultra-high-molecular-weight polyethylene by covalent coupling of lightly cross-linked polymer colloid particles [50% styrene, 49.8% (chloromethyl)stryrene, 0.2% divinylbenzene] to the interstitial pore surfaces. Swelling the covalently coupled colloid particles in a good solvent followed by chemical derivitization resulted in an immobilized pore-surface gel phase rich in primary amine groups. The macromolecular reactivity and molecular size-exclusion characteristics of the aminated pore-surface gel phase were then determined using monofunctional, amine-reactive, poly (ethylene glycol)s (PEG). Pegylated pore-surface gel phases that ranged from 71% (10,000 molecular weight PEG) to 56% (40,000 molecular weight PEG) PEG by weight resulted from reaction of the aminated gel phase with the PEG probe molecules. The number of PEG molecules reacting with the aminated pore-surface gel phase depends only on the Flory radius (or radius of gyration) of the PEG molecule to the negative 2.49th power i.e., $1/R_f^{2.49}$, corresponding to a $M^{-1.48}$ dependence. The immobilized and pegylated polymer colloid particles swell by a factor of 16–25 times the diameter of the original polymer colloid particles in water, thereby demonstrating that pegylation occurred though a substantial fraction of the volume of the immobilized colloid particles.

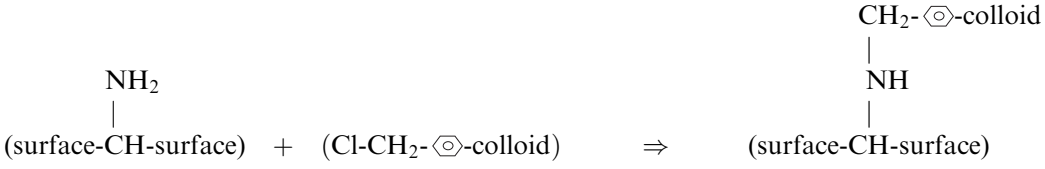
Key words Macroporous · Polymer colloid · Polymer surface chemistry modification · Polymer gels

Introduction

Pellicular monolith materials are produced by covalent coupling of specially designed polymer colloid particles [1] to the functionalized pore surfaces of macroporous ultra-high-molecular-weight polyethylene (UHMWPE). Solvent swelling and chemical derivitization of the covalently immobilized colloid particles results in a macroporous monolithic material containing a covalently immobilized pore-surface gel phase throughout the porous matrix. The pore surfaces of the otherwise inert macroporous UHMWPE are functionalized to enable covalent immobilization of the polymer colloid. Flowing discharge radical chemistry (FDRC) methods for the amination and oxidation of macroporous UHMWPE have been previously reported [2–6] as has the preparation and characterization of the pellicular monolith made from FDRC aminated UHMWPE [7]. Chemical derivitization of the covalently immobilized polymer colloid results in a pore-surface gel phase rich in accessible alkyl amine functionality. The macromolecular reactivity and molecular size-exclusion characteristics of the alkyl-amine-rich pore-surface gel phase are reported here as determined by measuring the extent of reaction with low polydispersity ($M_w/M_n < 1.06$) *N*-hydroxysuccinimide (NHS) esters of poly(ethylene glycol) (PEG) carboxylic acids. The water-swelling and fluid-flow characteristics of the pellicular monolith

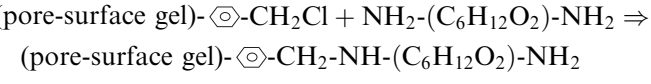
containing the pegylated, amine-rich pore-surface gel phase are also reported and reveal important aspects of the macromolecular architecture of the pellicular monolith following reaction with the high-molecular-weight PEG-NHS esters.

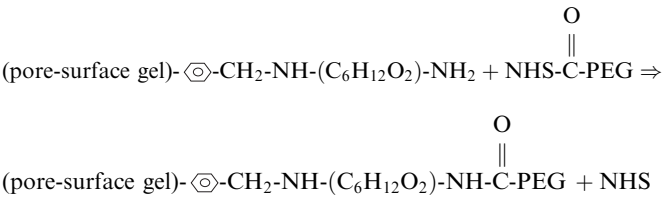
The polymer colloid used in this work was a copolymer of styrene, (chloromethyl)styrene, and divinyl benzene. The polymer colloid was prepared so that the composition was expected to be uniform through the cross-section of the colloid particles. A limited number of the benzyl chloride residues on the exterior of the colloid particles react directly with the alkyl amine functions on an FDRC aminated macroporous polyethylene material [7] to immobilize the colloid particles as shown below.



After covalent coupling to the aminated pore surfaces, the majority of the benzyl chloride groups interior to the polymer colloid particles are still available for chemical derivitization after swelling in a good solvent for polystyrene, such as tetrahydrofuran (THF), dimethylformamide (DMF), or toluene. The low degree of cross-linking internal to each polymer colloid particle prevents loss of polymer chains from the immobilized polymer colloid particles during swelling and derivitization. The mechanical support provided by the macroporous polyethylene framework enables the use of pore-surface gels with cross-linking values well below that needed to provide mechanical integrity to gel slabs or beads.

Derivitizing the benzyl chloride groups with triethylene glycol diamine results in a pore-surface gel phase rich in primary alkyl amines, as shown in the reaction schemes below. The aminated pore-surface gel phase is then characterized by reaction with a series of monofunctional PEG-NHS ester probe molecules [8], also shown in the reaction scheme below. The PEG-NHS esters are dissolved in THF, a good solvent for both PEG and the polystyrene-like polymer colloid, for this reaction. Well-known relationships between molecular weight and molecular size in dilute polymer solutions can then be used to estimate the size-exclusion characteristics of the pore-surface gel phase.





Both the derivitization of the benzyl chloride groups in the polymer colloid particles with triethylene glycol diamine, and the subsequent reaction of the amine-rich pore-surface gel phase with PEG-NHS ester probes were carried out in THF. THF was selected as the reaction solvent in this work because it is a good solvent for both polystyrene and PEG. The parameters of the Kuhn–Mark–Howink–Sakurada (KMHS) equation provide a useful index of solvent quality for many polymers [9]. Experimental values of the KMHS parameters for polystyrene and PEG in THF at 25 °C have been reported [10, 11] and are shown below, where η is the intrinsic viscosity and M_v is the viscosity-average molecular weight.

$$[\eta] = 6.09 \times 10^{-3} M_v^{0.79} \text{ ml/g for polystyrene [10]}$$

$$[\eta] = 3.49 \times 10^{-4} M_v^{0.66} \text{ ml/g for poly(ethylene glycol) [11]}$$

In both cases, the molecular-weight exponent is significantly greater than 0.5, the value predicted by theory for a θ solvent, and is in the range of values expected for "good" solvents, i.e., between 0.6 and 0.8 [9].

When THF is used as the mobile phase and polystyrene gel beads are used as the stationary phase in the gel permeation chromatographic (GPC) analysis of PEGs, the data show the absence of significant adsorptive interactions between PEG and polystyrene in THF [11]. Successful application of the well-known universal calibration relationships to the PEG retention time data confirms that the separation depends only on the hydrodynamic volume of the PEG polymers in THF [11].

The behavior of soluble macromolecules in gels is a subject of considerable practical interest and has recently been critically reviewed [12]. The average size of the flexible linear polymer in solution plays a key role in determining the equilibrium partitioning of the polymer molecule between free solution and a gel or other porous

medium [13, 14]. The average size of the flexible polymer in solution also has a profound effect on the number of polymer chains that can be covalently tethered to a surface and the properties of tethered polymer surface phases under various conditions [16–18]. In the work presented here, soluble polymers are covalently tethered to attachment points in a swollen gel matrix. As a result, the theories describing the equilibrium partitioning of polymer molecules between the solution and the gel phase, in the absence of any strong specific interaction between the soluble polymer and the gel [12], are not applicable to the work presented here and will not be considered further.

A general relationship between the average molecular size of a flexible linear polymer in a good solvent and the number of monomer units in the polymer chain is given by Eq. (1) [19]. The Flory radius, R_f, of a polymer molecule is a function of N, the number of monomer units in the polymer chain, and a_f, the effective length per monomer unit in the expanded chain [19]. The molecular weight of the polymer chain is simply $c \times N$, where c is the molecular weight of the repeat unit. Substituting the expression for the molecular weight in terms of N into Eq. (1), we obtain Eq. (2) that gives R_f in terms of the molecular weight.

$$R_f = a_f N^{0.588} \tag{1}$$

$$R_f = a_f c^{-0.588} (\mathrm{M})^{0.588} \tag{2}$$

The radii of gyration, R_g, of PEG molecules in good solvents have been observed to fit power laws having the general form of Eq. (2) [20–21]. Equation (3) results from fitting the light scattering data produced by several different groups in three good solvents (methanol, water, and acetonitrile) over a molecular-weight range of $2.2 \times 10^4 - 1.1 \times 10^6$ [20]. Equation 4 results from a static light scattering study in methanol [21] over a molecular-weight range of $8.6 \times 10^4 - 9.1 \times 10^5$. In both cases, the molecular-weight exponent is in reasonable agreement with both the 0.6 value predicted by Flory as well as the 0.588 value predicted by renormalization theory [19]. The R_g values for the reactive PEG-NHS esters used in this work (calculated with Eqs. 3, 4) are shown in Table 1.

$$R_g = 0.0202(\mathrm{M_w})^{0.55}\ \mathrm{nm} \tag{3}$$

$$R_g = 0.0143(\mathrm{M_w})^{0.61}\ \mathrm{nm} \tag{4}$$

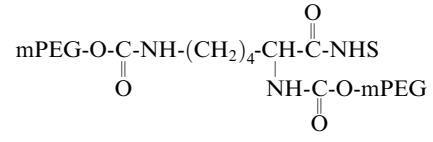
Materials, methods, and apparatus

Porex X-4920 (Porex Technologies, Fairburn,Ga., USA) was the macroporous UHMWPE material used in this work [1]. Porex X-4920 has a nominal pore size of 30 μm as measured by mercury intrusion porosimetry and a specific area of 1400 cm^2/g as measured by krypton gas adsorption as previously reported [7]. The pore-surface amination of Porex X-4920 using FDRC methods was achieved with apparatus and methods similar to those previously reported [2–7].

The polymer colloid was purchased as a custom synthesis product from Bang's Laboratories, Fishers, Ind. USA. The polymer composition was specified as 50% sytrene, 49.8% (chloromethyl)styrene, and 0.2% divinylbenzene with a particle size of 0.46 μm as a surfactant-stabilized colloidal dispersion in water (10% solids by weight). The polymer colloid suspension was dialyzed overnight against pH 8.0, 50 mM sodium phosphate buffer and was then diluted tenfold in fresh buffer before covalent coupling to the pore surfaces of the FDRC aminated Porex X-4920. The coupling reaction ran for 1 h at 55 °C.

Triethylene glycol diamine (Jeffamine XTJ-504) was obtained from Huntsman Chemicals (Austin, Tex., USA) and was used as received. Triethylene glycol diamine (5 g) was dissolved in 17.5 cm^3 dry, stabilized THF (OmniSolv, stabilized with 250 ppm butylated hydroxytolune, EM Science, Gibbstown, N. J., USA) and 2.5 cm^3 anhydrous DMF. (Aldrich Chemical Company, Milwaukee, Wis., USA) for derivitization of the benzyl chloride functions in the immobilized polymer colloid. The reaction of triethylene glycol diamine with the pore-surface immobilized colloid particles ran for 1 h at 55 °C. Colloid coupling was verified after the reaction with triethylene glycol diamine by measuring the dry-weight gain on the preweighed contents of two sample vials after extensive washing and extraction with THF.

Low polydispersity ($M_w/M_n < 1.06$) PEG-NHS esters were obtained from Shearwater Polymers (Huntsville, Ala., USA). The molecular properties of the PEG-NHS esters used in the work reported here are summarized in Table 1. The PEG-NHS esters were prepared by coupling monofunctional, low polydispersity PEGs to both the α and the γ amino groups of the amino acid lysine. The NHS ester functional group in the remaining PEGs was located midway between the termini of the linear PEG molecule. The molecular structure of these PEG-NHS esters is shown below.



Shearwater Polymers analyzed the PEG-NHS esters and a certificate of analysis was provided. NMR, UV-VIS and GPC measurements all indicated greater than 90% purity for the PEG-

Table 1 Shearwater poly(ethylene glycol) (*PEG*) polymer molecules

Shearwater PEG polymer (Shearwater catalog number)	Molecular weight	(M_w/M_n) GPC	R_g, (Eq. 3) (nm)	R_g, (Eq. 4) (nm)
PEG2NHS-10K	10,000	1.02	3.20	3.94
PEG2NHS-20K	20,000	1.02	4.69	6.01
PEG2NHS-40K	40,000	1.06	6.86	9.17

NHS esters with no evidence of polyfunctional PEG-NHS esters. The PEG-NHS esters were used as received.

The number of moles of PEG-NHS ester in each reaction mixture was held constant at 6.25×10^{-6} mol, while the number of moles of pore-surface gel phase amine was held constant at 12.5×10^{-6} mol so that the PEG-NHS ester was the limiting reagent for all experiments. The PEG polymers were dissolved in THF containing 1% (w/v) tributylamine (Aldrich Chemical Company, Milwaukee, Wis., USA) for reaction with the pore-surface gel phase. The tributylamine serves to assure deprotonation of the primary amines in the pore-surface gel phase while not reacting directly with the PEG-NHS esters itself. Reaction of the PEG-NHS esters with the aminated pore-surface gel phase was allowed to proceed for 72 h at room temperature, with stirring, in sealed vessels. The extent of PEG coupling to the aminated pore-surface gel phase was determined by measuring the dry-weight gain on duplicate reaction vials after extensive washing and extraction of the product with THF and water. High-purity water (18 MΩ cm) prepared on a Barnstead E-Pure water system (Barnstead, Dubuque, Iowa, USA) was used throughout.

The extraction procedure used to assure complete removal of noncovalently bound PEG from the PEG derivitized pellicular monolith materials involved three immediate washings with THF followed by three overnight extractions with THF and three overnight extractions with high-purity water. Forty milliliters of extraction or wash solvent was used in each extraction or wash step for each gram of pellicular monolith material. The washing/extraction procedure for the colloid coupling and amination step was similar but employed THF only. It should be noted that samples used for dry-weight determination after the colloid coupling and gel amination steps were not used in subsequent PEG-NHS ester reaction studies. Covalent bonding of the PEG-NHS esters was further verified in control experiments in which the NHS ester function was blocked by prior reaction of the PEG-NHS ester with excess 1-propylamine.

Results and discussion

The outcome of each PEG-NHS ester coupling reaction with the aminated pore-surface gel phase is shown in Table 2 as a function of PEG-NHS ester molecular weight. The results of coupling reactions between the PEG-NHS esters and FDRC aminated Porex (no pore-surface gel phase) are shown in Table 3. All the quantities in Tables 2 and 3 are normalized to 1 g ammonia FDRC Porex X-4920. Colloid coupling and derivitization of the immobilized colloid particles with triethylene glycol diamine resulted in a consistent dry-weight gain of 13.5 ± 1 mg aminated colloid particles per gram of ammonia FDRC Porex. The mass of PEG subsequently coupled to the pore-surface gel phase ranged from 35 to 17 mg PEG per gram of ammonia FDRC Porex. The weight gains from PEG coupling imply surface gel phase compositions ranging from 71 to 56% PEG by weight. Yields of the PEG coupling process (100% yield corresponds to complete binding of all PEG molecules by the twofold molar excess reactive groups in the aminated pore-surface gel phase) ranged from 6.5 to 0.85%. In all cases, the amount of PEG bound and the percentage theoretical yield decrease monotonically with increasing PEG molecular weight. The high PEG content of the pegylated pore-surface gel phase implies covalent binding of the PEG probes, either throughout the entire volume of the aminated pore-surface gel phase, or through a substantial fraction thereof. Reaction of the PEG-NHS esters with FDRC aminated Porex X-4920 material (no pore-surface gel phase) resulted in much smaller dry-weight gains and a monotonic decrease in the amount of PEG bound with increasing PEG-NHS ester molecular weight (Table 3). Blocking of the PEG-NHS ester by prereaction with 1-propylamine resulted in no significant dry-weight gain on reaction with either the FDRC Porex or the monolith containing the aminated pore-surface gel phase.

If all of the reactive amines in the pore-surface gel phase (or the ammonia FDRC Porex) were equally available to the PEG-NHS esters, irrespective of molecular weight, then the number of moles of PEG bound per gram of ammonia FDRC Porex and the percentage theoretical yield would be constant. As a result, the specific dry weight gain would increase proportionally to

Table 2 Reaction of PEG-*N*-hydroxysuccinimide (*NHS*) esters with the aminated pore-surface gel phase

PEG-NHS ester molecular weight	Weight (mg) of PEG bound per gram of Porex X-4920	Weight percent PEG in final pore-surface gel phase	Micromoles of PEG bound per gram of Porex X-4920	Percentage of theoretical yield
10,000	35.2 ± 1	71%	3.25 ± 0.1	6.5%
20,000	22.5 ± 1	62%	1.13 ± 0.05	2.3%
40,000	17 ± 0.5	56%	0.425 ± 0.012	0.85%

Table 3 Reaction of PEG-NHS esters with ammonia flowing discharge radical chemistry (FDRC) Porex

PEG-NHS ester molecular weight	Weight (mg) of PEG bound per gram of Porex X-4920	Micromoles of PEG bound per gram of Porex X-4920	Surface coverage σ (molecules/Å^2)
10,000	1.6	0.160	6.8×10^{-3}
20,000	0.7	0.035	1.5×10^{-3}
40,000	0.8	0.020	8.6×10^{-4}

the molecular weight. Inspection of the data in Tables 2 and 3 demonstrates that this outcome was not obtained. Instead, the specific dry-weight gain and the two quantities calculated from the specific dry-weight gain, i.e., the number of moles of PEG bound per gram of ammonia FDRC Porex and the percentage theoretical yield are all monotonically decreasing functions of PEG-NHS ester molecular weight.

The relationship between the molecular weight of the PEG-NHS ester and the number of moles of PEG bound per gram of ammonia FDRC Porex (with pore-surface gel phase) is plotted in the upper part of Fig. 1 (data points with error bars). The number of moles of bound PEG displays a simple power-law relationship with the PEG molecular weight. The molecular-weight dependence of PEG-NHS ester binding by the aminated pore-surface gel phase is best described by Eq. (5), which is plotted as the upper solid line in Fig. 1. Equation (5) was obtained by a nonlinear least-squares regression fit of the data in Table 2 to a power-law model. The correlation coefficient was −0.999 and the covarience was −0.969. Equation 5 (upper solid line) is plotted against the data in Fig. 1. If both sides of Eqs. (2)–(4) are taken to the −2.49 power we obtain molecular-weight exponents of −1.46, −1.37 and −1.52 respectively. The number of moles of PEG covalently bound by the amine-rich pore-surface gel phase and the percentage theoretical yield are, therefore, directly related to $R_f^{-2.49}$ or $R_g^{-2.49}$.

$$\text{MPEG(pore} - \text{surface gel)} = 2.371(\text{M})^{-1.47} \quad (5)$$

Similarly, the number of moles of PEG bound by 1 g ammonia FDRC Porex itself (no pore-surface gel phase) is plotted as a function of PEG molecular weight in the lower part of Fig. 1. The molecular-weight dependence of PEG-NHS ester binding by the ammonia FDRC Porex itself (no pore-surface gel phase) is best described by Eq. (6), which is plotted as the lower dashed line in Fig. 1. Equation (6) was obtained by a nonlinear least-squares regression fit of the data in Table 3 to a power-law model.

$$\text{MPEG (FDRC)} = 0.1363(\text{M})^{-1.50} \quad (6)$$

The number of moles of PEG-NHS ester tethered to the surface of ammonia FDRC Porex displays nearly the same molecular-weight dependence as the number of moles of PEG-NHS ester tethered to the pore-surface gel phase, though about 50 times less material was bound by the ammonia FDRC Porex. Referring back to Eqs. (1) and (2) we see that $M^{-1.47}$ corresponds to $N^{-1.47}$and to $R_f^{-2.49}$. Szleifer and Carignano [17] have shown that a single-chain mean-field (SCMF) theory treatment of polymer tethering ($N < 100$) leads to a universal adsorption isotherm. The universal adsorption isotherm relates the product of surface coverage, σ, and $N^{7/5}$ to a universal function of the chemical potential of the solution polymer chain, the tethered polymer chain, and the Boltzmann factor containing the energy of the tethering reaction. All else being equal, σ (proportional to the number of moles of PEG bound per gram of Porex) should decrease as $N^{-1.50}$, as observed in the present work for the bare aminated Porex surface. The fact that the number of moles of PEG bound by the pore-surface gel phase also depends on $N^{-1.47}$ supports the very reasonable conjecture that configurational entropy effects and simple steric crowding of PEG chains limit PEG tethering by the pore-surface gel phase in a similar way. It should be noted that SCMF theory has also been successfully applied to the tethering reaction of a polydimethylsiloxane with an M_w of 145 000, enabling accurate prediction of surface coverage as a function of polymer volume fraction in solution [17].

Tethering a random coil polymer to a surface or in other restricted environments is subject to steric crowding effects and configurational entropy penalties arising from the reduction in the number of possible chain configurations for the tethered chains compared to the free chains [16–18]. Increasing the number of grafted chains per unit area further increases the entropic penalty as interchain repulsion effects come into play eventually forcing the tethered chains to assume a brush-phase configuration [16–18]. The molecular-weight dependence of the PGE-NHS ester tethering reactions can be reasonably explained in terms of the steric crowding effects and energetic penalties of tethering linear chains to surfaces or in other restricted environments. There is no evidence that the PEG-NHS ester probe molecules were subject to simple gel phase filtration effects over the molecular weight range studied.

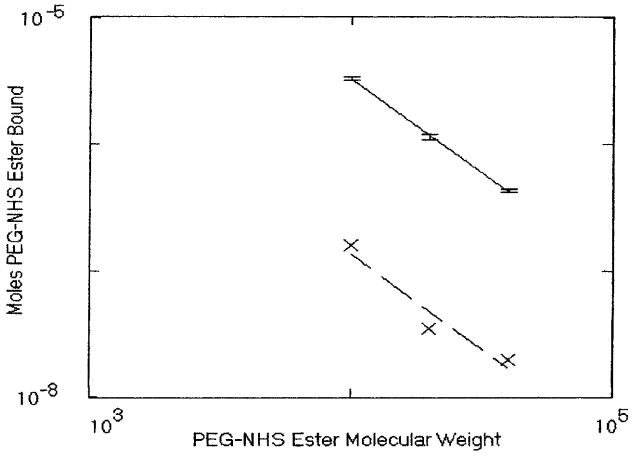


Fig. 1 Number of moles of polyethylene glycol–hydroxysuccinimide. (*PEG-NHS*) ester covalently bound by the aminated pore-surface gel phase contained in 1 g FDRC aminated Porex X-4920 (*upper plot*). The *error bars* represent data points and the *solid line* is Eq. (5) (see text). The *lower plot* shows the number of moles of PEG-NHS ester covalently bound by 1 g FDRC aminated Porex X-4920 (no pore-surface gel phase). The (+) symbols are data points and the *dashed line* is Eq. (6)

Table 4 Water-swelling properties by hydraulic radius measurement

Macroporous material	Hydraulic radius (μm)	Change in hydraulic radius relative to aminated Porex X-4920 (μm)
FDRC aminated Porex X-4920	23.9 ± 1	0
FDRC aminated Porex X-4920 + pegylated pore–surface gel phase PEG molecular weight = 10,000	14.0 ± 0.05	−9.9
FDRC aminated Porex X-4920 + pegylated pore-surface gel phase PEG molecular weight = 20,000	16.4 ± 1.3	−7.5
FDRC aminated Porex X-4920 + pegylated pore-surface gel phase PEG molecular weight = 40,000	17.4 ± 0.3	−6.5

The water-swelling properties of the various pegylated pore-surface gel phases implies that the PEG-NHS ester coupling reaction pegylated a significant fraction of the total volume of the aminated pore-surface gel phase. Measurement of the flow rate of water through short columns of aminated Porex and the pegylated monolith materials made from that aminated Porex show that the pegylated materials have somewhat smaller pore sizes (Table 4). The smaller pore size is a direct result of water-swelling of the pegyalted pore-surface gel phases.

Measurement of the flow rate of water, driven by a known hydrostatic pressure head, through a porous material of known geometry permits direct calculation of the hydraulic radius of that porous material [7, 16, 17]. The results of hydraulic radius measurements on FDRC aminated Porex and the corresponding pegylated pellicular monolith materials are shown in Table 4. The reduction of the hydraulic radius in water, relative to FDRC aminated Porex X-4920, is between 6 and 10 μm and correlates with the PEG content of the pore-surface gel phase. Given that the initial diameter of the polymer colloid particles in aqueous suspension was 0.46 μm, a swelling factor or the order of 16–25 times is indicated, in water, as a result of pegylating the pore-surface gel phase. It is well known that polystyrene-*co*-(chloromethyl)styrene does not dissolve or swell in water. The high degree of water swelling exhibited by the pore-surface gel phase, following pegylation, suggests that the pegylation reaction proceeded uniformly throughout the immobilized polymer colloid particles, and was not limited to a small region near the particle surface.

Summary and conclusions

Covalent immobilization of a lightly cross-linked polymer colloid on the functionalized pore surfaces of a macroporous UHMWPE material produces a pore-surface gel phase of substantial thickness, high gel porosity, and high amine content, when the immobilized polymer colloid particles are swollen and derivitized. The aminated pore-surface gel phase can react efficiently with low-polydispersity PEG-NHS esters with molecular weights between 10 000 and 40 000 to yield pegylated pore-surface gel phases containing 71–56% PEG by weight. The relative amount of PEG bound by the pore-surface gel phase depends very nearly on $R_f^{-2.49}$. Reasoning by analogy with models of tethered polymer layers on surfaces, the $R_f^{-2.49}$ dependence may be expected if the yield of the PEG-NHS ester tethering reaction depends only on the configurational entropy penalties that arise from tethering polymer chains in the restricted environment.

The pegylated pore-surface gel phases show water-swelling factors of 16–25 times relative to the diameter of the starting polymer colloid particles. Taken together, the high PEG content of the pegylated materials and the large water-swelling factors suggest that the pegylation reaction proceeded throughout most of the volume of the aminated pore-surface gel phase, not just near the surface of the original polymer colloid particles. The data demonstrate that the low degree of cross-linking designed into the polymer colloid particles is retained on covalent immobilization and derivitization. Finally, the pegylated pellicular monolith retained useful fluid flow properties, as shown by the changes in the hydraulic radius, compared to the macroporous UHMWPE starting material, and showed no evidence of plugging or other severe degradation of fluid flow properties.

One of the original motivations for developing the pellicular monolith was to provide a convenient format for the use of polymer gel phases having unusually low degrees of cross-linking and high degrees of swelling. Conventional polymer gel formats, such as cross-linked beads or slabs require some minimum degree of cross-linking to provide mechanical stability during use. In the pellicular monolith, the macroporous polymer provides mechanical support for the pore-surface gel phase that can then have the minimum degree of cross-linking needed to prevent dissolution of the gel. Construction of the pore-surface gel phase by covalent immobilization and derivitization of specifically designed polymer colloids allows control of the thickness of the final pore-surface gel phase relative to the pore diameter of the macroporous support material. As a result, the resulting pellicular monolith retains useful fluid flow and mass transfer properties important for applications in the areas of solid-phase synthesis, chromatography, and catalysis.

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