

Formation and Characterization of Covalently Bound Polyelectrolyte Brushes

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Poly(4-vinylpyridine) (PVP), functionalized at one terminus with a styrenyl group, was end-grafted to vinyl-functionalized self-assembled monolayers by UV irradiation in 1-methyl-2-pyrrolidinone. In this solvent and with oxygen excluded, surface reactions appeared to be selectively limited to the polymer terminus. The dry film thickness was determined by ellipsometry and the grafted amount by FTIR-ATR (Fourier transform infrared spectroscopy in attenuated total reflection). Controlled amounts of positive charge were introduced into the grafted chains by alkylation with a 2.5% solution of CH₃I in dimethylformamide (DMF). FTIR-ATR was used to quantify the extent of alkylation, from 10% to 96%. These polyelectrolyte brushes will comprise a model system for studying polyelectrolytes at surfaces.

Introduction

Not enough is understood about the behavior of *electrically charged* polymer chains at surfaces. The interplay is complex between charge density on the chain, chain connectivity, and long-standing mysteries regarding counterion distribution and counterion condensation. This imperfect understanding impedes progress in not only fundamental polymer physics but also applications in related applied fields, from biomaterials to membrane separations and food science. In approaching these problems experimentally, polymer “brushes”—chains end-grafted to a surface at one end, the rest dangling into solution—comprise an attractive model system. There are many exciting recent developments in the theory and simulation of polyelectrolyte brushes,^{1–7} but experiments are few, largely due to the paucity of experimental methods to form securely-anchored polyelectrolyte chains with narrow molecular weight distribution.

In past work, polyelectrolyte brushes have been produced by the adsorption of hydrophilic–hydrophobic diblock copolymers from aqueous solution, but with this approach permanent attachment is not ensured.⁸ Surface graft polymerization of charged monomers and step-growth approaches⁸ are also possible,^{9–13} but chains prepared by this approach are polydisperse. In an approach similar in spirit to the one that we outline below to produce grafted cationic brushes, Mir and co-workers end-grafted polystyrene chains to silicon and then sulfonated the phenyl rings,¹⁴ producing a grafted brush carrying negative charge.

Here, we introduce a simple and versatile method to generate end-grafted chains of the cationic polymer, quaternized poly(4-vinylpyridine), on a variety of solid substrates. We show that the grafting density and charge density can be controlled over a wide range.

Strategy

In initial experiments we sought to graft chains to Si wafers by the formation of Si–C bonds, following the approach introduced for small molecules by Chidsey and co-workers.¹⁵ Although chains can in principle be end-grafted by this method, physisorption of segments elsewhere on the chain comprised a serious problem since even a modest tendency to stick per segment (such that the corresponding monomeric repeat unit could be easily rinsed off) adds up to an overwhelmingly-large tendency to stick per polymer molecule. It was found necessary to protect the solid surface against physisorption. A suitable method to create a nonadsorbing surface of low surface energy is to create close-packed, well-ordered organic monolayers. Figure 1 summarizes our final synthetic strategy: we chemically reacted a styrenyl-terminated polymer chain to a self-assembled monolayer containing mixed methyl and olefin functionality at the terminus and subsequently modified the uncharged polymer to the polyelectrolyte form.

To begin with, monolayers were formed on the substrate surface (silicon or mica) by allowing hydrolyzed octadecyltriethoxysilane, mixed in the proportion 3 to 1 by weight with hydrolyzed 19-icosenyltriethoxysilane (OLE), to self-assemble from a dilute hydrocarbon solution. The self-assembly methods to do this were described previously.¹⁶

For subsequent grafting to these functionalized surfaces, styrenyl-terminated poly(4-vinylpyridine) (PVP), synthesized by anionic polymerization and terminated by vinylbenzene chloride, was purchased from Polymer Source (Québec, Canada). As reported by the company from gel permeation chromatography (GPC), the weight-average molecular weight was $M_w = 6000$ (degree of polymerization of 60) and the ratio of weight-average to number-average molecular weight $M_w/M_n = 1.17$. The degree of functionality, determined by the company using NMR spectroscopy, was 0.88.

UV Excitation and Deposition Procedure. The light source was a small pencil Hg (Ar) lamp (Oriel Model 6035, average intensity $\sim 4500 \mu\text{W}/\text{cm}^2$ at a distance of 2.5 cm) that is sold for calibration of optical spectrometers. It possesses a wide range of ultraviolet (UV) lines of known wavelength-dependent intensity.^{17,18} The 253.65 nm line is most intense, and the intensity at other wavelengths is orders of magnitude less.¹⁸ This UV

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(1) Chen, H.; Zajac, R.; Chakrabarti, A. *J. Chem. Phys.* **1996**, *104*, 1579.

(2) Zhulina, E. B.; Birshtein, T. M.; Borisov, O. V. *Macromolecules* **1995**, *28*, 1491.

(3) Israëls, S.; Leermakers, F. A. M.; Fleer, G. J.; Zhulina, E. B. *Macromolecules* **1994**, *27*, 3249.

(4) Borisov, O. V.; Zhulina, E. B.; Birshtein, T. M. *Macromolecules* **1994**, *27*, 4795.

(5) Pincus, P. *Macromolecules* **1991**, *24*, 2912.

(6) Misra, S.; Varanasi, S.; Varanasi, P. P. *Macromolecules* **1989**, *22*, 4173.

(7) Miklavic, S. J.; Marčelja, S. *J. Phys. Chem.* **1988**, *92*, 6718.

(8) Amiel, C.; Sikka, M.; Schneider, J. W., Jr.; Tsao, Y.-H.; Tirrell, M.; Mays, J. W. *Macromolecules* **1995**, *28*, 3125.

(9) Zhang, J.; Uchida, E.; Uyama, Y.; Ikada, Y. *Langmuir* **1995**, *11*, 1688.

(10) Zhou, Y.; Bruening, M. L.; Bergbreiter, D. E.; Crooks, R. M.; Wells, M. J. *Am. Chem. Soc.* **1996**, *118*, 3773.

(11) Wilkie, C. A.; Suzuki, M.; Dong, X. X.; Deacon, C.; Chandrasiri, J. A.; Xue, T. J. *Polym. Degrad. Stab.* **1996**, *54*, 117.

(12) Ulbricht, M.; Riedel, M.; Marx, U. *J. Membr. Sci.* **1996**, *120*, 239.

(13) Yang, W. T.; Ranby, B. *Polym. Bull.* **1996**, *37*, 89.

(14) Mir, Y.; Auroy, P.; Auvray, L. *Phys. Rev. Lett.* **1995**, *75*, 2863.

(15) Linford, M. R.; Fenter, P.; Eisenberger, P. M.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1995**, *117*, 3145.

(16) Peanasky, J.; Schneider, H. M.; Granick, S.; Kessel, C. R. *Langmuir* **1995**, *11*, 953.

(17) Sansonetti, C. J.; Salit, M. L.; Reader, J., *Appl. Opt.* **1996**, *35*, 74.

(18) Reader, J.; Sansonetti, C. J.; Bridges, J. M. *Appl. Opt.* **1996**, *35*, 78.

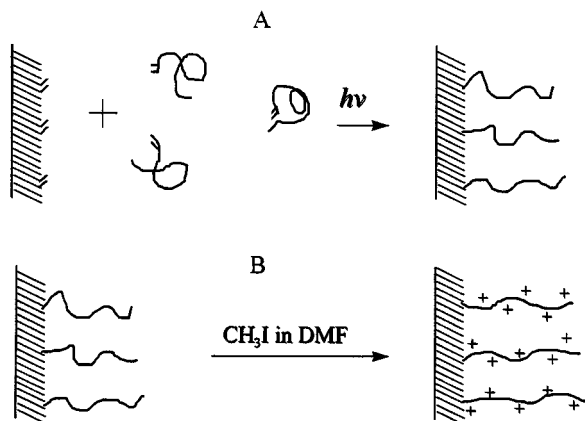


Figure 1. Strategy to form an end-grafted polyelectrolyte brush. First (A) styrenyl-terminated poly(vinylpyridine) (PVP) in 1-methyl-2-pyrrolidinone (MP) was grafted onto vinyl-terminated organic monolayers through exposure to ultraviolet (UV) radiation as described in the text. Next (B) the grafted PVP layer was quaternized by reaction with methyl iodide in dimethylformamide (DMF).

radiation was directed onto the sample through a N_2 atmosphere from a distance of 1.0 cm.

Deposition was usually performed from solutions of PVP in 1-methyl-2-pyrrolidinone (MP) at room temperature. The solutions were purged with dry N_2 for at least 30 min before exposure to UV radiation. The solvent, MP, is a thermodynamically good solvent for PVP. A key point is that the strong absorption band of MP (its UV absorptivity is $2900 \text{ M}^{-1} \text{ cm}^{-1}$ at the absorption peak, 205 nm ¹⁹) acted as a low-wavelength filter for UV radiation. This protected the polymer from exposure to high-energy radiation that otherwise would be expected to cause random cross-linking of the polymer chains through hydrogen abstraction.

The data (see below) are consistent with the interpretation that radiation caused selective UV excitation of the styrenyl terminus of the functionalized PVP. This happened, we believe, due to the adsorption of light by the terminal styrene ring, followed by migration of this energy to the terminal olefin group. The hypothesis is reasonable because the absorptivity of the styrene ring is high ($12\,900 \text{ M}^{-1} \text{ cm}^{-1}$ at 251 nm ; $900 \text{ M}^{-1} \text{ cm}^{-1}$ at 282 nm ; $500 \text{ M}^{-1} \text{ cm}^{-1}$ at 291 nm ²⁰).

Note that the high extinction coefficient of PVP groups (about $2000 \text{ M}^{-1} \text{ cm}^{-1}$ at 257 nm) and their high concentration in solution imply that this photochemically-induced radical formation was limited to a thin layer close to the solution surface. A simple calculation shows that the intensity of UV radiation at 253 nm should decrease by 6 orders of magnitude as it passed through a $300 \mu\text{m}$ layer of a 1 wt % solution of PVP in MP.

In this work we used two alternative setups for grafting:

Method I. The substrate was separated from the UV lamp by the reactant PVP solution of thickness less than $10 \mu\text{m}$. This solution was sandwiched between the substrate and a precleaned quartz window through which the UV radiation was directed.

Method II. The substrate was slowly dipped through the gas-liquid interface of the reactant PVP solution, while UV radiation was directed onto this interface. The dipping rate was approximately 0.5 mm s^{-1} . With this approach one can use the volume selectivity of the UV activation to produce surface patterning.

In both cases, after deposition, the substrates were rinsed with MP and then with ethanol and dried with nitrogen gas. After quaternization, the substrates were rinsed in DMF and ethanol and dried with dry nitrogen. Similar grafting and quaternization procedures should also be effective for grafted poly(2-vinylpyridine).

Quaternization of the Grafted Polymer Chains. Methods to alkylate PVP in bulk solution are well-known,²¹⁻²³ and these same methods were found to be effective for the alkylation of

chains when grafted. The coated surfaces were immersed in a 2.5% solution of CH_3I in dimethylformamide (DMF) at room temperature for controlled times. Under these conditions, the rate of alkylation was slow to the point that good control of the degree of quaternization was possible simply by controlling the reaction time.

Parenthetically, it is worthwhile to note the failure of our early attempts to quaternize these brushes using ethyl bromide (at $60 \text{ }^\circ\text{C}$) in methanol and, to a lesser extent, in DMF. We found that the alkylation from this reaction was not permanent; infrared characterization (see below) showed that the PVP chains reverted to the uncharged state after exposure to H_2O . A plausible mechanism is that ethyl bromide in alcohol solution did not produce only ethyl-alkylated PVP but instead partially protonated polymer, as found long ago by Fuoss and Strauss.²¹ This side reaction may be favored at a surface. Some amount of thermal decomposition at $60 \text{ }^\circ\text{C}$ may also occur.²¹ Upon subsequent exposure to water, quaternization by protonation would be reversible and neutral polymer would be recovered.

Ellipsometric Characterization. The measurements were performed on dry films in air using a Gaertner Model L116C ellipsometer with He/Ne laser (632.8 nm) illumination at a 70° angle of incidence. Thickness was calculated using Gaertner software for one layer assuming fixed refractive indices of 1.46 for SiO_2 , 1.48 for the self-assembled monolayer, and 1.55 for the grafted PVP layer. The thickness of each of these successively-produced layers was measured after measuring the real and imaginary parts of the refractive index of the substrate bearing the previously-deposited layer, n_s and K_s . The solid substrates were Si (100) wafers. For the effective formation of OTE monolayer films the silicon must be pretreated by the controlled growth of an oxide layer, as described previously.¹⁶ In the present experiments the thickness of the grown oxide, determined by ellipsometry, was from 30 to 50 \AA .

It is worth emphasizing the robustness of these calculations. If one were to assume (unrealistically) the same refractive index of 1.46 for all three layers, taking silicon as the substrate, one would overestimate the thickness of the self-assembled monolayer and of the grafted polymer film by only 2% and 6%, respectively.

Infrared Characterization. The instrument was a Biorad FTS 60A Fourier transform infrared spectrometer (FTIR), employed in the mode of attenuated total reflection (ATR). Spectra were collected in a dry nitrogen atmosphere at 4 cm^{-1} resolution using 512 averaged scans. The grafted amounts were determined from the calibrated bulk absorbance of PVP solutions of known concentration in D_2O . The Si ATR crystal was a Si (100) $50 \times 20 \times 2$ trapezoidal crystal with a 45° angle of incidence (Harrick Corp., Ossining, NY).

Results and Discussion

Grafting. It may be seen from comparing parts A and B of Figure 2 that the same limiting density of surface coverage was obtained from deposition methods I and II. The film thickness and the amount grafted on the self-assembled monolayer were determined independently from ellipsometry and FTIR-ATR, respectively, with excellent agreement, assuming the density of PVP = 1.0 g cm^{-3} .

In Figure 2A, one sees that the dry thickness and the grafted amount grew at first in proportion to the number of dipping cycles and leveled off after 10. An example of FTIR-ATR measurement (the skeletal in-plane vibration at 1597 cm^{-1}) is shown in the inset of Figure 2A. From the measured grafted amount and the known molecular weight of grafted chains, the grafting density in this example is readily calculated to be $1.5 \times 10^{13} \text{ chains cm}^{-2}$. This corresponds to an average spacing of 26 \AA between chains that is only slightly larger than the estimated average dimension of the Gaussian unperturbed PVP chain in solution, 23 \AA (though Gaussian statistics may hardly be applicable to molecules with so few segments in the chain).

(19) Korte, F.; Lihmer, K. H. *Chem. Ber.* **1958**, *91*, 1397.

(20) Newell, J. E. *Analyt. Chem.* **1951**, *23*, 445.

(21) Fuoss, R. M.; Strauss, U. P. *J. Polym. Sci.* **1948**, *3* (2), 246.

(22) Margolin, A. L.; Izumrudov, V. A.; Svedas, V. K.; Zezin, A. B.; Kabanov, V. A.; Berezin, I. V. *Biochim. Biophys. Acta* **1981**, *660*, 359.

(23) Schwab, F. C.; Hellwell, I. J. *Ind. Eng. Chem. Product Res. Dev.* **1984**, *23*, 435.

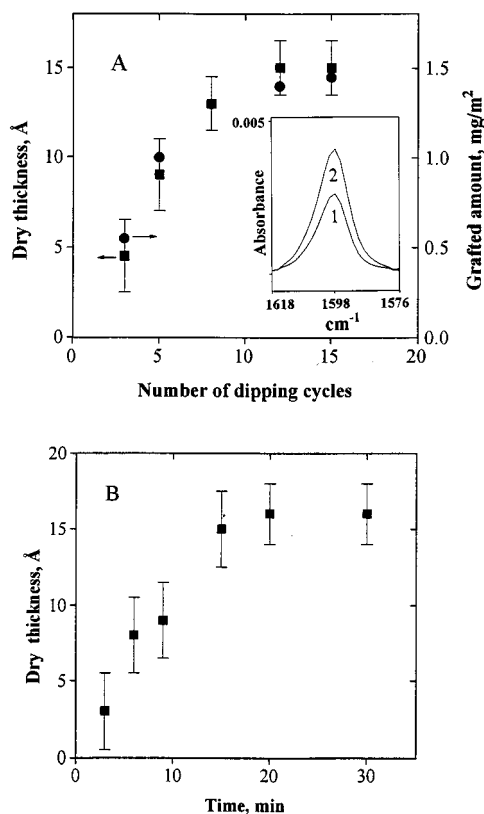


Figure 2. Plots showing the amount of PVP grafted onto silicon using deposition methods I and II. The reactant solution was 10 mg mL^{-1} PVP in MP. (A) The grafted amount determined by infrared spectroscopy (circles, right axis) and the ellipsometric thickness (squares, left axis) is plotted against the number of dipping cycles with deposition method II. Inset: Infrared absorption peak of the skeletal in-plane vibration at 1597 cm^{-1} of the carbon–nitrogen vibration in the pyridine ring of PVP, used to determine the grafted amount. The absorption peak illustrates that the integrated peak intensity was proportional to the grafted amount. The lines illustrate (1) grafted PVP at 60% of maximum surface coverage and (2) grafted PVP at 90% of maximum surface coverage. (B) For deposition method I, ellipsometric thickness is plotted against the time of exposure to UV illumination.

It is interesting to notice that the rate of grafting by method I (Figure 2B) was much slower than would be expected from simply the diffusion of chains to the surface. It is likely that particular orientations of the macromolecule terminus toward the interfacial olefin group were required for reaction to proceed. Another factor likely to slow down the kinetics is that the quantum yield of the self-initiated olefin–olefin coupling is known to be much less than unity.²⁴

Figure 3 shows the dependence of the grafted amount on the PVP solution concentration. This saturated at 2 mg m^{-2} at concentrations above 2–2.5 wt % PVP and corresponds to the grafting density of 2×10^{13} chains cm^{-2} and the chain spacing of 22 \AA . For the layers formed by irradiation through PVP solutions $2 \mu\text{m}$ thick, the ratio of free to grafted polymer would be 20 at this point of saturation. This suggests consumption of PVP molecules in the bulk solution, presumably by UV-induced disproportionation and/or coupling reactions between PVP molecules. The inert molecules produced by these side reactions should not interfere with the surface grafting reaction.

Control experiments were also performed, in which the solid substrates coated with self-assembled monolayers

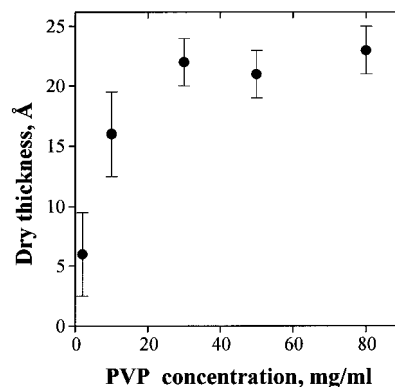


Figure 3. Dependence of the grafted amount on PVP concentration in MP solution. The ellipsometric thickness is plotted against the PVP concentration for deposition by method I.

were exposed to a 1 wt % PVP solution in MP under the standard conditions except without UV irradiation. In this case the quantity of adsorbed polymer was immeasurably small ($<0.1 \text{ mg m}^{-2}$, within the experimental uncertainty). This experiment showed that the accumulation of polymer at the interface, shown in Figure 2, was due to grafting reactions. In another control experiment, a 1 wt % solution of PVP in MP was exposed to a methyl-terminated self-assembled monolayer and illuminated by UV light. No grafting resulted, thus proving the participation of surface olefin functional groups in the grafting reaction.

Regarding the grafting mechanism, at present there is insufficient experimental evidence to distinguish between mechanisms of $2 + 2$ cycloaddition and radical addition. The main point is that the terminal styrenyl group on the PVP appears to be sufficiently photoactive to continue a chain of excitation initiated by photoexcitation. Cycloaddition to simple olefins in solution has been reported.^{25,26} On the other hand, a radical mechanism of grafting is also plausible: the reaction would not run away at a surface because a polymer chain, attached at one end to the solid surface, should sterically hinder the diffusion of a second polymer chain to this point of attachment. This should suppress the rate of chain propagation and make more probable termination of the monoadduct radical by hydrogen abstraction from a solvent molecule or by recombination with a solvent radical. In comparing expectations for surface and bulk reactions, it is certainly true that, due to a reduced incidence of favorable collisions by the reactants, fixing the olefin group to the surface should reduce the quantum yield, but the large excess of styrenyl-terminated PVP that we used assured a high degree of grafting.

Alkylation. FTIR-ATR was used to characterize the extent of alkylation. The in-plane C–N peak of pyridine shows a large shift in absorption frequency upon alkylation, from 1597 to 1641 cm^{-1} . As shown in Figure 4, these peaks are well-separated in the infrared spectrum and their relative intensities provide a convenient measure of the extent of alkylation. In these experiments, calibration was easy because the IR peak of the charged polymer grew at the expense of the IR peak of the neutral polymer. The ratio of absorptivity of charged to neutral units is known to be 1.68.²⁷

(25) Arnold, D. R.; Baird, N. C.; Bolton, J. R.; Brand, J. C. D.; Jacobs, P. W. M.; de Mayo, P.; Ware, W. R. *Photochemistry: An Introduction*; Academic Press: New York, 1974; pp 169–171.

(26) Rabek, J. F. *Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers*; Wiley: New York, 1987.

(27) Izumrudov, V. Private communication.

(24) Odian, J. *Principles of Polymerization*; John Wiley and Sons: New York, 1981; p 206.

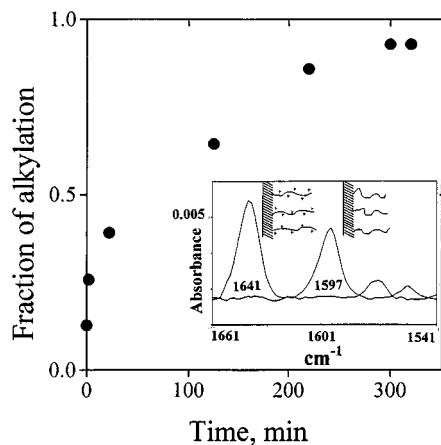


Figure 4. Dependence of the degree of alkylation on the time of exposure to 2.5% CH_3I in DMF. The degree of alkylation was controlled from 10% to 96%. Inset: Infrared absorption peaks of the carbon-nitrogen vibration in the pyridine ring of neutral PVP (1597 cm^{-1}) and of the quaternized pyridine ring (1641 cm^{-1}). Smaller satellite peaks are also visible at 1558 and 1573 cm^{-1} , respectively. Schematic diagrams of the alkylated and neutral grafted chains are drawn near each infrared peak.

Figure 4 shows that the extent of alkylation with CH_3I under the conditions described above could be conveniently controlled over a wide range, from 10% to 96%, simply by varying the reaction time from 10 min to 5 h. An important point is that the alkylated layers were stable in water for long periods of time. Control experiments showed that <5% of the grafted chains desorbed when the substrates were kept in water for 12 h at room temperature. This was probably due to penetration of water through defects in the monolayer to Si–O–Si linkages at the surface and their hydrolysis.

It is interesting to consider also the uniformity of alkylation. Though we have no direct experiment evidence concerning this, the rate of alkylation is known to be slowed down by charge–charge interactions (this is why it is so difficult to achieve 100% alkylation of PVP), so we expect homogeneous lateral distribution of charge. The question of whether alkylation might be inhomogeneous from outside to inside the brush layer is more difficult to answer in principle (this might occur if the concentration of methyl iodide during the reaction were less in the inner layer than the outer), but 98% alkylation could be achieved. On this basis we conclude that “slowing down” of alkylation adjacent to the surface was not significant, though its possibility cannot be excluded completely.

Other Solid Substrates. Although we present in this paper data only for deposition onto Si, the assembly of polyelectrolyte brushes on muscovite mica, glass, and other oxide surfaces can be accomplished by the same protocols described in this paper after the surface has been functionalized with OLE monolayers; the methods to form OLE monolayers have already been described.¹⁶ The resulting layers are suitable as a model system for surface patterning by lithography, for *in-situ* X-ray reflectivity measurements of counterion distribution, and for measurements of brush thickness and shear nanorheology in a surface forces apparatus. Studies in these directions are in progress.

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