Surface Modification of Poly(dimethylsiloxane) Microfluidic Devices by Ultraviolet Polymer Grafting

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Poly(dimethylsiloxane) (PDMS)-based microfluidic devices are increasing in popularity due to their ease of fabrication and low costs. Despite this, there is a tremendous need for strategies to rapidly and easily tailor the surface properties of these devices. We demonstrate a one-step procedure to covalently link polymers to the surface of PDMS microchannels by ultraviolet graft polymerization. Acrylic acid, acrylamide, dimethylacrylamide, 2-hydroxyethyl acrylate, and poly(ethylene glycol)monomethoxyl acrylate were grafted onto PDMS to yield hydrophilic surfaces. Water droplets possessed contact angles as low as 45° on the grafted surfaces. Microchannels constructed from the grafted PDMS were readily filled with aqueous solutions in contrast to devices composed of native PDMS. The grafted surfaces also displayed a substantially reduced adsorption of two test peptides compared to that of oxidized PDMS. Microchannels with grafted surfaces exhibited electroosmotic mobilities intermediate to those displayed by native and oxidized PDMS. Unlike the electroosmotic mobility of oxidized PDMS, the electroosmotic mobility of the grafted surfaces remained stable upon exposure to air. The electrophoretic resolution of two test peptides in the grafted microchannels was considerably improved compared to that in microchannels composed of oxidized PDMS. By using the appropriate monomer, it should be possible to use UV grafting to impart a variety of surface properties to PDMS microfluidics devices.

Polymer-based microfluidic devices are rapidly gaining in popularity primarily due to their ease of fabrication, inexpensive costs, and increasing versatility.¹–³ These devices have been fabricated from a variety of different polymers including poly(methyl methacrylate) (PMMA), polycarbonate, polystyrene, and poly(dimethylsiloxane) (PDMS). In particular, PDMS-based devices can easily and inexpensively be fabricated by casting the polymer against a mold prior to cross-linking.⁴,⁵ Since the casting step does not require access to a cleanroom, this methodology is accessible to a large number of investigators. The low Young’s modulus and durability of PDMS make it an excellent choice for fabrication of pumps and valves.⁶–⁹ Additionally, PDMS readily seals with itself as well as many other materials such as glass and PMMA. PDMS has also been utilized in the “rapid prototyping” of devices designed for electrophoretic separations.⁵ Despite these advantages, systems fabricated from PDMS exhibit a number of weaknesses that must be overcome before PDMS can be considered the material of choice for microsystems employing electrophoresis.⁵,¹² These disadvantages are as follows: (1) the extreme hydrophobicity of PDMS makes the devices difficult to fill with aqueous solutions, (2) the strong tendency to adsorb other molecules onto the surface with some molecules actually migrating into the polymer matrix itself, and (3) the unstable and poorly controlled electroosmotic flow. A variety of solutions, primarily surface modifications, have been proposed, for example, oxygen plasma treatment, silanization, adsorbed coatings (Polybrene/dextran sulfate), and protein or lipid coatings.⁹,¹³,¹⁷–¹⁹ However, surface modifications such as oxygen plasma treatment and
adsorbed coatings can be unstable requiring periodic reapplication. Protein-based coatings frequently result in ill-defined and heterogeneous surface properties as proteins are attached in a multiplicity of orientations with some molecules denatured and others folded. Other surface coatings require difficult multistep procedures or modification of the running buffer solution making them undesirable. A library of easily applied, covalently attached coatings with selectable surface properties would greatly enhance the utility of PDMS as a substrate for electrophoretic-based microdevices.

Surface modifications, both chemical and physical, are in widespread use to tailor the surface properties of polymers for biomedical applications. These applications include coatings for catheters, prostheses, grafts, and other implants. Typical goals are a decrease in biomolecular adsorption, an increase in the hydrophilic or hydrophobic character of the surface, the attachment of a biologically active molecule, or an alteration in the lubricity of the surface. The polymer surface is modified by roughening, oxidation, application of coatings (adsorbed and other), ion implantation, and graft polymerization. Graft polymerization in particular has seen widespread use throughout polymer chemistry. Typically it involves creation of reactive sites (radicals) on the polymer surface followed by covalent linkage of a preformed polymer or more commonly a monomer that can then be used as the initiation site for a polymeric chain. Radicals on a previously inert polymer surface are created by application of chemical reagents or by exposure to ionizing radiation or ultraviolet (UV) light. UV graft polymerization is highly attractive as a method for the surface modification of microfluidic devices since it has few steps and possesses low or no penetration into the bulk polymer. Silicone rubbers including PDMS have successfully been modified by radiation-induced grafting. In the case of PDMS, an initial reaction with a photosensitizer was required before UV grafting could be accomplished. More recently, Ikada and colleagues demonstrated that under the appropriate conditions some polymers (nylon, polypropylene, poly(ethylene terephthalate), polyethylene) can be UV-grafted in a one-step reaction without photoinitiators or radicals on a previously inert polymer surface. Under the appropriate conditions some polymers (nylon, polypropylene, poly(ethylene terephthalate), polyethylene) can be UV-grafted in a one-step reaction without photoinitiators or photosensitizers.

In this paper, novel hydrophilic PDMS-based microfluidics chips were prepared by UV graft polymerization using the Ikada method. This simple one-step procedure can be used to impart a variety of different surface properties to PDMS. We demonstrate the preparation of hydrophilic coatings on PDMS. The properties and success of the coatings were investigated by measuring the graft density, contact angle, and infrared absorption by total attenuated reflection (ATR-IR) spectra of the surfaces. The ability of the tailored surfaces to interact with other materials was characterized by assessing their ability to seal with other materials and to adsorb kinase substrate peptides. The suitability of the coatings for use in electrophoretic devices was determined by quantifying the electroosmotic mobility (μeo), measuring the stability of μeo, and electrophoresing two model analytes.

**EXPERIMENTAL SECTION**

**Reagents.** Sylgard 184 was purchased from Dow Corning (Midland, MI), and silicon nitride-coated silicon wafers were obtained from Wafernet Inc. (San Jose, CA). Acrylic acid (AA), acrylamide (AM), N,N-dimethylacrylamide (DMA), 2-hydroxyethyl acrylate (HEA), poly(ethylene glycol) monomethoxyl acrylate (PEG), and benzyl alcohol were all obtained from Aldrich and used without further purification. All fluorescent reagents were purchased from Molecular Probes (Eugene, OR). Peptides were synthesized by the Beckman Peptide and Nucleic Acid Facility at Stanford University (Stanford, CA) and labeled with fluorescein as described previously. The peptide sequences were fluorescein-Arg-Phe-Ala-Arg-Lys-Gly-Ser-Leu-Arg-Gln-Lys-Leu-Asn-Val (F-PKC) and fluorescein-Ala-Glu-Glu-Glu-1le-Tyr-Gly-Glu-Phe-Glu-Ala-Lys-Lys-Lys-Lys-Lys-Lys-Lys-Lys-Lys-Lys-Lys-Lys-Lys-Lys-Val (F-src). All other reagents and materials were purchased from Fisher Scientific (Pittsburgh, PA).

**Device Fabrication.** Microfluidic channel patterns and the corresponding master were designed and fabricated as described previously. Sylgard 184 PDMS prepolymer was mixed thoroughly with its cross-linking catalyst at 10:1 (w/w) and degassed by vacuum. The polymer was cast against the silicon mold and polymerized at 70 °C for 1 h. After curing, the PDMS was peeled from the mold and holes (3.4 mm diameter) were punched into the polymer to create access ports and reservoirs. Flat PDMS substrates were obtained by casting the polymer mixture on a clean, flat surface. Final polymerization of the PDMS was performed by placing the pieces in a 65 °C oven overnight. The micromolded PDMS was sealed against a flat, PDMS substrate. In some instances, the unmated PDMS halves were placed in an oxygen plasma for 30 s at 60 W for 20 min. When joined together, the oxygen plasma-treated parts sealed irreversibly. Alternatively, the two PDMS halves were grafted with a polymer as described in the next section and then mated.

**Surface Graft Polymerization.** Micromolded or flat PDMS films were immersed in an aqueous solution containing NaOCl (0.5 mM), benzyl alcohol (0.5 wt %), and monomer at the indicated concentration. The immersed films were placed in a custom-built irradiator (200 W mercury lamp) for the times indicated. The distance between the sample and the lamp was 5 cm. Uniform UV exposure was ensured by rotating the films under the UV source. The samples were then washed in distilled water at 80 °C under constant stirring for 24 h to remove adsorbed monomer and polymer.

**Measurement of Graft Density.** To dry PDMS films, they were placed under a vacuum at room temperature until the weight was stable. Dried PDMS films were weighed before and after
surface grafting. The graft density was defined as the difference in the film weight before and after grafting divided by the total surface area of the film.

Measurement of Infrared Absorption by Total Attenuated Reflection. ATR-IR spectra of PDMS films on a wedged germanium crystal were recorded using a single-beam spectrometer (Nicolet Magna-IR 860 spectrometer) equipped with a helium-neon laser, a triglycine sulfate (TGS) detector, and a ZnSe reflection element. Spectra were recorded at 4-cm⁻¹ resolution, and 4096 scans were collected per trace. A single-beam reference spectrum of a freshly cleaned germanium crystal was recorded before the measurements and used as the background spectrum. A water spectrum was also recorded, scaled empirically, and subtracted from the PDMS spectra to remove the water peaks in the region of 3500 cm⁻¹.

Measurement of the Contact Angle. Contact angles were measured on flat PDMS films with varying surface graft densities. A droplet of deionized water was placed on the air-side surface of a film at room temperature, and after 30 s, the contact angle was measured using a contact angle goniometer (NRL-100, Rame-Hart). The average of five measurements was utilized for each droplet.

Measurement of μeo. The current monitoring method was used to measure μeo in the microfabricated channels. Measurements were performed as described previously. Four measurements were performed on each device. A single straight channel 3 cm in length was used for the measurements. The channel’s width at the bottom, middle, and top was 30, 60, and 75 μm, respectively. The channel was 15 μm deep in the center. To measure the stability of μeo after exposure to air, the channels were flushed with water, dried under vacuum, and then exposed to air at room temperature. At the times indicated, the channels were filled with aqueous buffer and μeo was measured. After the measurement, the channels were flushed with water, dried under a vacuum, and again exposed to air at room temperature until the next measurement of μeo.

Measurement of Peptide Adsorption. PDMS films were spotted with either F-PKC or F-src (20 μM in 20 mM KH₂PO₄ (pH 7.0), 8 μL) in three separate locations. Two different films were utilized for each measurement. The films were incubated for 2 h and then washed extensively with water (20 mL). Fluorescent images of the films were recorded with a cooled CCD camera (Photometrix Coolsnap FX, Roper Scientific Inc., Tucson, AZ) mounted on an inverted fluorescence microscope (Nikon, Melville, NY). The integration time was 1 s. The average fluorescence intensity of the regions spotted with peptide was calculated using Metaflour (Universal Imaging Corp., Downingtown, PA).

Electrophoresis of Peptides. For electrophoretic injections, channels with a double-“T” injector were used (Figure 5A).32,33 The channels possessed curved sidewalls and were 15 μm deep at their center. The channel width at the bottom, middle, and top was 30, 50, and 80 μm, respectively. The lengths of the channels were as follows (see Figure 5): i—v, 1 cm; ii—v and iii—vi, 2 cm; iv—vi, 2.5 cm; v—vi, 140 μm. The electrophoretic buffer was Tris (25 mM, pH 8.4) and glycine (192 mM). All solutions were degassed by sonication for 10 min immediately prior to use. For sample injection, F-PKC or F-src (5 μM) was loaded into reservoir ii and then electrophoresed toward reservoir iii (reservoir ii at 500 V; reservoir iii at ground). The voltages applied to reservoirs i and iv (340 and 400 V, respectively) during injection prevented leakage of the sample plug into channels i—v and vi—iv. To inject the plug of sample contained in channel v—vi into the main electrophoresis channel (vi—iv), the voltages applied to the reservoirs were rapidly switched (reservoir i at 100 V; reservoirs ii, iii, and iv at ground). The power supplies (Ultravolt, Long Island, NY) used to apply the voltages were computer-controlled by custom software (Testpoint, Keithley-Metrabyte, Taunton, MA). The fluorescence of the channel (vi—iv) just prior to reservoir iv was imaged with a CCD camera as described in the previous section. The integration time was 1 s.

Atomic Force Microscopy. PEG-grafted films were placed under a vacuum at room temperature until the weight was stable. The dried films were then imaged with an atomic force microscope (Topometrix TMX 2010) in contact mode.

RESULTS AND DISCUSSION
Surface Grafting of Polymers onto PDMS. To modify the surface properties of PDMS devices, a variety of monomers were UV-grafted onto the PDMS surface. With this method, attachment of polymers can be accomplished in a single step. The monomers were selected to be hydrophilic since this is an attribute of most surfaces resistant to protein adsorption (compared to hydrophobic surfaces).19–21 The monomers, AA, AM, HEA, PEG, and DMA, were also selected based on their likely ease of attachment, past usage in biocompatible devices, and display of different functional groups.18–21 PDMS films were immersed in aqueous solutions containing the monomer and then irradiated with a mercury lamp. NaIO₄ was included in the monomer solution to scavengen oxygen, which could compete with the monomer for reaction with free radicals on the PDMS surface.25 The ultraviolet lines of the mercury lamp provide the energy to create radicals on the surface of the PDMS (Figure 1). Many investigators have shown that creation of the surface radicals initiates the attachment of the monomer to the surface, which is then followed by a self-propagating chain reaction (until termination) to yield the final polymer strand. Initial attempts at surface grafting onto the PDMS films, however, were unsuccessful using the above conditions. The surface density of grafted polymer on to the PDMS surface was unmeasurable irrespective of the concentration of monomer or NaIO₄ or the duration of UV exposure. Under these conditions, homopolymerization in the aqueous solution surrounding the film resulted in a highly viscous solution. The resulting restriction on the diffusion of reactive species to the surface may have further hindered efficient surface grafting.

Ikada and co-workers have shown that inclusion of benzyl alcohol in the monomer solution can substantially increase the efficiency of surface grafting.22,24 For the grafting of AA onto polyethylene, the efficiency of grafting increased as the concentration of benzyl alcohol increased.22 It is thought that benzyl alcohol may act as a chain-transfer agent during polymerization. Inclusion of benzyl alcohol facilitates chain termination, which greatly diminishes the viscosity of the aqueous solution, enhancing
diffusion of reactive monomer and polymer molecules to the PDMS surface. Addition of benzyl alcohol (10%) to the monomer/NaIO₄ solution during UV exposure greatly increased the grafting efficiency onto PDMS for all five monomers (PEG, DMA, AA, AM, HEA). To determine the quantity of monomer grafted, the graft density was measured after exposure to ultraviolet irradiation for varying times (Figure 2). The graft density for all monomers increased with the irradiation time; however, the rate of grafting was initially slow. This was most likely due to the time required to form sufficient numbers of radicals on the PDMS film to graft measurable quantities of monomer (either directly to the surface or as part of a growing chain). By 4 h, the rate of monomer addition to the films with the highest graft densities (AA, AM, HEA) had slowed markedly, probably due to increasing numbers of chain termination reactions and the filling of the available reaction sites on the films. The densities of AA, AM, and HEA are comparable to those measured for UV grafting of acrylamides onto poly(ethylene terephthalate), polypropylene, and other polymers. Lower graft densities (at a given concentration of monomer) were achieved for PEG and DMA compared to AA, AM, and HEA. Higher absolute graft densities could be obtained by increasing the monomer concentration of PEG and DMA. The lower relative graft densities of PEG may be due to the high viscosity of the PEG-containing solution. The solubility of poly-DMA in an aqueous environment decreases as the DMA chain length increases. Therefore, the lower relative graft density of DMA may be due to the exclusion of water near the surface of the PDMS as the DMA chain increased in length and degree of surface coverage. Increasing the concentration of benzyl alcohol increased the graft density for all of the monomers. At high graft densities (>100 μg/cm²) of AA, AM, HEA, and DMA, the films became less transparent to light and less flexible compared to native PDMS. This suggests that the grafted layer was sufficiently thick to begin to display the bulk properties (rather than just the surface properties) of the grafted polymer.

Surface Properties of Grafted PDMS. To determine whether the appropriate chemical groups were present on the surface of the grafted PDMS, the ATR-FITR spectra of the surface was measured. HEA- and PEG-grafted PDMS possessed absorption maximums at 1730 cm⁻¹, which corresponds to the carbonyl adjacent to the ester group in the grafted polymers (Figure 3A). Surfaces grafted with either DMA or AM displayed peaks centered at 1655−1660 cm⁻¹, which is due to the carbonyl groups adjacent to the amide group (Figure 3B). PDM surfaces grafted with AA exhibited a strong absorption at 1715 cm⁻¹ due to the carbonyl near the hydroxyl (Figure 3A). Native PDMS displayed no absorption bands between 1800 and 1500 cm⁻¹, suggesting that the PDMS was successfully linked to the different grafted polymer groups.

The contact angle measurement of a water droplet is frequently used as a measure of the hydrophobicity of a surface. To follow changes in the surface hydrophobicity of the PDMS during grafting, the contact angle of a water droplet was measured after varying exposure times to the UV light. The contact angle of unmodified PDMS was 109°, consistent with its high hydrophobicity. For all monomers grafted, the contact angle diminished over time, reaching a minimum at ~3.5 h (Figure 3C). The relative ordering of the contact angle achieved by 3.5 h was consistent with the density of surface grafting. For example, AA, which was deposited at the highest density, also produced the smallest contact angle (45°) or most hydrophilic surface. The high polarity of the AA monomer is also likely to increase the hydrophilic character of the surface as more monomers are attached. In contrast, PEG even after 3.5 h of grafting resulted in a contact angle close to 80° and a surface more hydrophobic than any other monomer used. PEG was also deposited at the lowest density, and it is possible that exposed regions of PDMS may contribute to the greater hydrophobicity of the grafted surface compared to

Figure 1. Reaction scheme for UV graft polymerization on a PDMS surface. Step I illustrates the formation of radicals on the PDMS surface by UV light. Step II displays the initiation step in the polymerization reaction. R is the monomer side group.

Figure 2. Effect of UV exposure time on the graft density. The concentration of the monomers (closed square, PEG; open square, DMA; closed circle, HEA; open circle, AM; triangle AA) was 10% (by weight). The data points are the average ± standard deviation of measurements from four different grafted films. In most instances, the height of the error bars was less than that of the symbols.

Figure 3. ATR-FITR spectra of the grafting process. 34 PDMS surfaces grafted with either DMA or AM displayed peaks centered at 1655−1660 cm⁻¹, which is due to the carbonyl groups adjacent to the amide group (Figure 3B). PDM surfaces grafted with AA exhibited a strong absorption at 1715 cm⁻¹ due to the carbonyl near the hydroxyl (Figure 3A). Native PDMS displayed no absorption bands between 1800 and 1500 cm⁻¹, suggesting that the PDMS was successfully linked to the different grafted polymer groups.

that of the other monomers. Additionally, when compared to the other grafted groups, the poly-PEG would be the more hydrophobic in nature.

Since PEG was deposited at the lowest density compared to other monomers, multiple regions (1 μm²) of a dried, PEG-grafted surface (5.8 g/cm²) were imaged by atomic force microscopy. No defects deeper than 1.5 nm or wider than 10 nm were seen. Based on the density of the dried PEG deposited on the surface and the density of solid PEG (1.2 g/mL), the minimum possible thickness of the PEG layer was calculated to be 50 nm. Thus, it seems unlikely that large regions of exposed PDMS are present on the surfaces.

**Adsorption of Peptides onto the Grafted PDMS.** To determine how the grafted polymers influenced the adsorption of biologically relevant peptides on to the PDMS surface, two fluorescently tagged peptides were spotted onto the surface of PDMS films. Both peptides are substrates for a kinase, F-PKC for protein kinase C and F-src for src kinase.29,30 These peptides are frequently used in in vitro and in vivo assays for kinase activity, and similar substrate peptides have been employed to measure kinase activity using glass and polymer microfluidic devices.35 Native, oxidized, and grafted PDMS films were incubated with the peptides and then thoroughly washed. The fluorescence of the films was then imaged and the degree of peptide adsorption quantitated from the residual fluorescence. The peptides that possessed a positive charge displayed minimal adsorption to the native PDMS or the grafted PDMS surfaces (Table 1). In contrast, the peptides remained on the surface of the oxidized PDMS even after extensive washing, suggesting that the peptides were very tightly adsorbed to the surfaces.

**Fabrication and Characterization of Devices for Electrophoresis.** To determine how the surface-grafted polymers influence the adhesiveness of the two PDMS halves of a microdevice, the top and bottom portions of a device were grafted with the monomers. Neither the starting PDMS surface nor the grafted surface was oxidized. At all graft densities PEG- and HEA-coated PDMS readily sealed with other like-coated surfaces. AM- and DMA-grafted surfaces sealed with like surfaces only at lower graft densities (<100 g/cm²). This was most likely due to the rigidity of PDMS films with high AM or DMA graft densities. All surfaces that did seal sealed reversibly, suggesting that the adhesiveness was due to a noncovalent interaction. The differential adhesiveness of the different surfaces may have been due to a number of other factors in addition to the PDMS flexibility, for example, the rotational mobility of the methyl and grafted polymers about the -Si-O- backbone of the PDMS at the surface and the properties of the grafted side chains themselves. Oxidation of the grafted surfaces was not attempted. Consequently, it is not known whether it is possible to irreversibly seal the devices.

**Measurement of μeo of Grafted PDMS Microchannels.** To determine how the grafted polymers altered electroosmotic fluid

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**Table 1. Fluorescence of PDMS Films after Adsorption of Peptide**

<table>
<thead>
<tr>
<th>Peptide</th>
<th>PDMS surface</th>
<th>AM</th>
<th>DMA</th>
<th>HEA</th>
<th>PEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-PKC</td>
<td>native</td>
<td>180±30</td>
<td>1100±150</td>
<td>290±10</td>
<td>400±40</td>
</tr>
<tr>
<td></td>
<td>oxidized</td>
<td>200±20</td>
<td>300±20</td>
<td>210±10</td>
<td>260±10</td>
</tr>
<tr>
<td>F-src</td>
<td>native</td>
<td>200±20</td>
<td>1500±200</td>
<td>200±10</td>
<td>280±20</td>
</tr>
<tr>
<td></td>
<td>oxidized</td>
<td>210±10</td>
<td>150±10</td>
<td>110±10</td>
<td>250±20</td>
</tr>
</tbody>
</table>

Each data point is the average ± standard deviation of six different experiments. The films were grafted with 10% monomer for 3 h.

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flow in microchannels, $\mu_{eo}$ was measured in channels grafted with varying densities of the monomers. As the graft density increased, $\mu_{eo}$ increased for all monomers tested (Figure 4A). For reference, $\mu_{eo}$ of native and oxidized PDMS was $0.8 \times 10^{-4}$ and $4 \times 10^{-4}$ cm$^2$/V·s, respectively. The increased value of $\mu_{eo}$ for the grafted polymers relative to that of native PDMS is expected since these surfaces are considerably more hydrophilic than native PDMS. The increase in magnitude of $\mu_{eo}$ began to plateau at graft densities near $\sim 30$–$60 \mu g/cm^2$, suggesting that higher densities did not substantially alter the $\zeta$ potential of the surfaces. The maximum $\mu_{eo}$ achieved at high densities of the AM-based polymer was $3 \times 10^{-4}$ cm$^2$/V·s. Not surprisingly, $\mu_{eo}$ of these polymers was always below that of oxidized PDMS, which possesses substantial negative charge. For any given graft density, grafted PEG had the lowest $\mu_{eo}$. The residual electroosmotic flow of the PEG-grafted PDMS is most likely attributable to the polar oxygen groups ($[-O-C-C-]_n$) of the polymer, which can behave in a manner similar to the oxygen groups of crown ethers. However, we cannot rule out an effect of the negatively charged PDMS below the PEG layer.

**Stability of $\mu_{eo}$ of Grafted PDMS Microchannels.** A major difficulty with the use of oxidized PDMS microchannels is the instability of $\mu_{eo}$ upon exposure of the devices to air. The decrease in $\mu_{eo}$ is thought to be due to the movement of hydrophobic groups to the PDMS surface either by reorientation of hydroxyl groups into the bulk and methyl groups to the surface or by the diffusion of low molecular weight PDMS from the bulk to the surface. The surfaces of other polymers can also be sufficiently dynamic to alter their properties in response to changes in the surrounding environment. For example, the surface of poly(hydroxyethyl methacrylate) films exposes methyl groups at polymer–air interfaces. Upon addition of water, however, the surfaces exhibit hydroxyl groups (instead of methyl groups) at the polymer–water interface. To determine the stability of the surfaces of the grafted microchannels, $\mu_{eo}$ was measured at varying times after exposure to air (Figure 4B). For the grafted devices, $\mu_{eo}$ was stable for up to 30 h (the longest time measured) irrespective of whether the devices were stored in air or water. In contrast, when microchannels with oxidized surfaces were exposed to air, $\mu_{eo}$ decreased by 30%.

**Electrophoresis on Grafted PDMS Microchannels.** To determine whether the grafted surfaces were suitable for electrophoretic applications, a microfluidics device with a double-T injector was constructed from PEG- and DMA-grafted PDMS as well as oxidized PDMS (Figure 5A). Oxidized PDMS was used rather than native PDMS due to the difficulty in filling unmodified PDMS devices with aqueous buffers. F-PKC and F-src were electrophoresed in the devices and the fluorescence of the peptides was detected 2 cm from the double-T with a CCD camera. When the two peptides were electrophoresed simultaneously in the oxidized PDMS channels, a single peak was always present with substantial peak tailing (Figure 5B). No separation of the peptides (or an impurity in the F-src; see below) was ever achieved despite the trial of multiple different separation conditions. When F-PKC was electrophoresed alone in the oxidized PDMS channels, no or very small peaks were detected. In addition, after F-PKC was injected, the channel between the sample and waste reservoirs (ii–v–vi–iii) were brightly fluorescent and remained so even after extensive washing. Following injection of the F-PKC plug from the double-T (v–vi) into the main electrophoresis channel (vi–iv), the main electrophoresis channel became fluorescent as the plug moved through the channel until the plug itself disappeared. Adsorption of this peptide to the oxidized PDMS was so severe that most of the sample was consumed before the sample could reach the detection zone. In contrast, when F-PKC and F-src were injected and electrophoresed in DMA or PEG-grafted channels, the sample to waste channels (ii–v–vi–iii) were nonfluorescent when the sample was pulled back into reservoirs ii and iii. Furthermore, the main electrophoresis channel (vi–iv)

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did not become fluorescent as the sample plug migrated through the channel and three peaks were always detected at the detection window (Figure 5C). The first peak (detected at 37 s) was due to F-PKC, and the second peak (50 s) was that of F-src. The peaks were identified by electrophoresing each peptide alone. A small peak (55 s) was consistently seen when F-src was electrophoresed alone or in combination with F-PKC, suggesting that it was an impurity contained in the F-src preparation. The separation efficiency of the positively charged peptides was dramatically improved in the grafted channels.

CONCLUSIONS

We have demonstrated a simple one-step method to graft the surface of PDMS with a variety of different monomers. The measurable graft density and the presence of the appropriate chemical groups observed by ATR-IR illustrated the successful attachment of AA, AM, HEA, DMA, and PEG to the surface of PDMS. For all monomers, grafting occurred only in the presence of benzyl alcohol, which is thought to act as a chain-transfer agent. All grafted surfaces exhibited a decrease in the contact angle of water compared to that of native PDMS. Consistent with the increased hydrophilic nature of the grafted surfaces, microchannels formed from the grafted PDMS were easily filled with aqueous solutions. At low graft densities (<100 μg/cm²), the PDMS films retained the flexibility and optical transparency of unmodified PDMS. These films also sealed reversibly so that devices constructed from them could be taken apart, cleaned, and resealed. $\mu_{\text{eo}}$ for the grafted microchannels was intermediate to that of native and oxidized PDMS, suggesting that the surfaces possessed a greater charge density than native PDMS but less charge density than oxidized PDMS. At high graft densities (>100 μg/cm²), some of the films became less flexible and exhibited a loss of transparency. However, $\mu_{\text{eo}}$ reached a maximum at graft densities less than 60 μg/cm², suggesting that full surface coverage had been attained. Thus, graft densities greater than 60 μg/cm² may only increase the depth of the polymer layer and not the extent of surface coverage. These higher graft densities may not impart any additional advantageous properties to the PDMS surfaces. Compared to oxidized PDMS, the grafted PDMS exhibited substantially less adsorption of charged, test peptides and a greatly improved separation efficiency of the peptides. Also in contrast to oxidized PDMS, $\mu_{\text{eo}}$ of the grafted PDMS devices was stable upon exposure of the channels to air. The decreased adsorption and increased surface stability of the grafted PDMS make these surfaces more suitable for many electrophoretic applications. By combining UV-mediated grafting with the appropriate monomer, it should be possible to impart a large number of different surface properties to PDMS thereby greatly increasing the utility of PDMS in the construction of microfluidic devices.

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