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Convenient Method for Modifying Poly(dimethylsiloxane) with Poly(ethylene glycol) in Microfluidics

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This report describes a convenient and reproducible method for the covalent modification of poly(dimethylsiloxane) (PDMS) with poly(ethylene glycol) (PEG) chains to suppress nonspecific protein adsorption. PEG additives terminated with a vinyl group are added into the PDMS prepolymer; when the PDMS is thermally cured, the vinyl group reacts with the silane groups on the PDMS, which covalently link the PEG group to the PDMS network. The PEG-modified PDMS surfaces are characterized with FT-IR, X-ray photoelectron spectroscopy (XPS), and contact angle measurement. We also examined the modified PDMS for on-chip capillary electrophoresis and its capability of resisting nonspecific protein adsorption using bovine serum albumin (BSA) as a model. Based on our study, a molecular mechanism is given to successfully explain the surface properties of the modified PDMS surfaces.

Poly(dimethylsiloxane) (PDMS) has become the most popular and versatile material in microfluidics and other areas as well.[1−7] Compared with other chip materials such as glass, silicon, and plastics, including PMMA and PC, PDMS offers some unique advantages: easy fabrication, elastomeric (which is critical for the generation of efficient mechanical microvalves), optically transparent, biologically inert and nontoxic, permeable to gases, and ready to seal with other materials.[1,7,8] However, the property of the native PDMS surface can often create problems for its applications in microfluidics.[9,10] For example, its hydrophobic surface makes it difficult to fill microchannels with aqueous solutions, and its uncharged surface cannot support enough electroosmotic flow (EOF) for electrophoresis separations.[11] In addition, various protein molecules are easy to stick to a native PDMS surface through nonspecific adsorption, causing fouling of the surface and loss of protein analytes from solutions.[12,13] Such surface fouling and protein loss are unwanted in biorelated applications such as microchip heterogeneous immunoassays, bioseparations, and cell-based bioassays. Therefore, the surface properties of PDMS are often required to be modified.[14−18]

Among all materials that are used for resisting protein nonspecific adsorptions, poly(ethylene glycol) (PEG) has been shown to be probably the most effective and reliable.[19−22] PEG-containing moieties have been widely used to modify PDMS surfaces in microfluidics either by physical adsorption or through covalent bonding.[23−28] A typical example of physical adsorption is that poly(L-lysine)-graft-poly(ethylene glycol) copolymers (positive charged) are adsorbed onto an oxygen-plasma-treated PDMS surface (negative charged) through the electrostatic interactions of the lysine residues in the polymer and the oxidized PDMS surface.[23] Another method simply mixes PEG copolymers with PDMS precursors; after the PDMS pieces are cured, the PEG copolymers will be trapped in the PDMS matrix and some of the

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PEG chains are expected to be present at the surface.[29] The physical adsorption method is usually simple and fast to perform. However, the strength of physical adsorptions is highly susceptible to the conditions of its surrounding solution (e.g., ionic strength, pH, and applied voltages in CE separations), and the PEG polymers can slowly be lost to the solution. In comparison, covalent bonding gives more robust surface modification. Generally, the PDMS surface is activated via oxygen plasma or oxidative acid treatment to create a thin layer of silica; PEG-containing molecules are then covalently bonded to this silica layer through various coupling reactions.[30−32] Covalent bonding of PEG gives a highly stable modification. However, the modifications often involve organic solvents, which swell the PDMS network and are usually avoided.[33]

Alternatively, Zare et al. demonstrated that PDMS prepolymers can conveniently react with vinyl groups containing additives (amine and carboxylic acid) to tune the electroosmotic mobility of PDMS microchannels.[34] We also previously showed that a hydroxyl group can also be exploited for generating highly fluorescent PDMS.[35] Here, we adapt this strategy to modify the PDMS surface with PEG through covalent bonding by directly copolymerizing vinyl-containing PEG chains onto the PDMS network. Because of the long length and hydrophilicity of the PEG chain, the molecular details on the surface can be different from those with small molecules. Because the cross-linking of PDMS is based on the reaction between −Si−H and −Si−CH=CH_2, the PEG additive molecules are covalently bonded with the PDMS matrix through the vinyl bond during curing. We examined the changes of PDMS surface properties before and after PEG modification from different aspects. We found that this modification can increase the hydrophilicity of the surface, slightly increase electroosmotic mobility of PDMS surface, and effectively suppress nonspecific protein adsorption on the surface. A small amount of sodium dodecyl sulfate added in the CE running buffer can dramatically increase the EOF and support successful separations. On the basis of our results, we proposed a molecular model to illustrate the PEG arrangement at the PEG-modified PDMS surface.

EXPERIMENTAL SECTION

Materials and Equipment. The PDMS prepolymer was from GE Silicones RTV615 (GE). Poly (ethylene glycol) methyl ether methacrylate (PEGMEM, MW∼475), fluorescein sodium, rhodamine 6G, and other chemicals were purchased from Aldrich. Fluorescein labeled bovine serum albumin was purchased from Invitrogen, Inc. Sodium dodecyl sulfate, Na_2HPO_4, and NaH_2PO_4 were obtained from Shanghai Chemical Reagents Corporation (Shanghai, China). All reagents were of analytical grade and used without further purification. X-ray photoelectron spectroscopy was performed with a Model PHI 5600 (peak positions normalized to the carbon peak at 284.5 eV). Contact angles were measured with a JC2000A contact angle analyzer (Shanghai Zhongchen Digital Technology and Equipment Co., Shanghai, China) at room temperature. A fluorescence microscope (AZ100, Nikon) was used to observe all fluorescent samples by recording with a microscope digital camera (DS-Fi1, Nikon). Fluorescence images of all fluorescent samples were collected with a green filter (excitation: 490−500 nm, emission: 520−560 nm).

FT-IR Measurement. Fourier transform infrared (FT-IR) spectra were recorded using a Spectrum One spectrometer (Perkin-Elmer) at resolution of 4 cm^{-1}. Samples were prepared by spin-coating on clean silicon wafers at 2500 rpm for 1 min (thickness ∼5 um) and being cured at 70 °C overnight. The unreacted PEGMEM is extracted by soaking in $CHCl_3$ for 5 h (refresh 3 times). After chloroform is removed, the sample membranes were placed onto KBr pellets for FT-IR characterization. PEGMEM was added on a KBr pellet and spread to be a thin layer by blowing N_2.

Microchip Fabrication. Chip fabrication was adapted from procedures previously reported.[36] For fabricating a PEG modified PDMS chip, different components were mixed thoroughly and poured over silicon masters (prepared with photolithography). After degassing, PDMS was cured at 70 °C for 12 h. The cured PDMS was peeled from the master, and holes were punched as reservoirs. Flat PDMS pieces were obtained by casting a corresponding prepolymer on clean wafers. Cured PDMS pieces were sealed reversibly with each other with conformal contact to form enclosed chips. The separation channels are ∼200 μm in width and ∼100 μm in depth.

Capillary Electrophoresis (CE) Measurement on Chip. The microchip electrophoresis was carried out under a fluorescence microscope with a CCD camera for recording. High voltages were provided by a home-built high-voltage power supplier controlled by a PC running custom software created with LabView (National Instruments, Austin, TX). The separation is performed in a 10 mM phosphate buffer (pH 7.4, with or without sodium dodecyl sulfate additive) with a separation electric field of 200 V/cm. Fluorescent signals were collected with a CCD camera (DS-Fi1, Nikon) mounted on a fluorescence microscope (AZ100, Nikon). The fluorescence intensity of a line profile along the separation channel was analyzed with the NIS Elements BR 3.0 software (Nikon), and the electropherogram was constructed by plotting fluorescence intensity against migration distance.

Derivatization of Proteins and Amino Acid. The cytochrome c (Cyt c), lysozyme, and lysine solutions (20 mg/mL) were prepared individually in 10 mM sodium bicarbonate (pH 9.2). The fluorescent derivative reagent, fluorescein isothiocyanate (FITC), was dissolved in dimethyl sulfoxide (DMSO) at 15 mg/mL just before use. The FITC solution was then mixed with protein/amino acid solutions at a molar ratio of 4:1, and the reaction was allowed to proceed at room temperature for 2 d in the dark. Prior to analysis, the derivatized protein solutions were purified by centrifugation.

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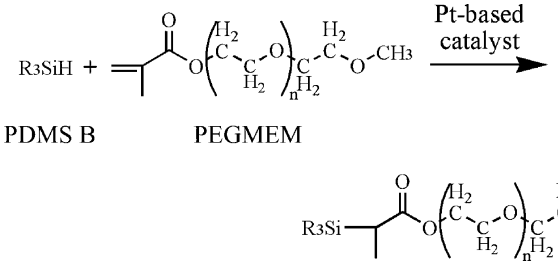
Scheme 1. Reaction of PEGMEM with PDMS Component B



RESULTS AND DISCUSSION

Modification of PDMS with Vinyl-Terminated PEG by Covalent Bonding. To modify the PDMS surface with PEG chains, we chose poly(ethylene glycol) methyl ether methacrylate (PEGMEM) as the additive material because of three reasons: (1) this molecule has a linear structure with a terminating vinyl group; (2) it is liquid at room temperature, making it easy to mix homogeneously with PDMS prepolymers; and (3) it is inexpensive and commercially available from common chemical companies. Scheme 1 illustrates the polymerization reaction of PDMS curing. The silane group has also been shown to be able to react with other unsaturated groups such as the vinyl group on PEGMEM in the presence of a Pt catalyst under the thermal curing process.[37] This hydrosilylation reaction covalently bonds the PEG to the cross-linked PDMS networks; accordingly, some PEG groups are presented on the surface of the cured PDMS. This modification process avoids organic solvents, which is environmental friendly and greatly decreases the experimental cost and time.

We follow the normal ratio of the two PDMS components (A and B) at 10:1 and tune the ratio of PEGMEM for making PDMS pieces. When the mass ratio PEGMEM additive is no more than 1.0% in the mixture, the PEG−PDMS can be cured in the same condition (70 °C, ~0.5 h) as native PDMS (without any PEGMEM additive); the resulting PEG−PDMS has similar mechanical properties as natively cured PDMS. A higher percentage of PEGMEM makes it more difficult to cure the mixture; a longer curing time or higher temperature is required. For example, it takes half an hour at 120 °C to fully cure 3.0 wt % PEGMEM-doped PDMS and at 200 °C to cure 10 wt % PEGMEM-doped PDMS. Even a higher percentage of PEGMEM turns the mixture uncurable. We also examined the influence of the PDMS prepolymer part B on the curing process of the doped PDMS. Although the PDMS prepolymer part B contains a Si−H bond, which reacts with the vinyl bond and bonds the PEG chain to the PDMS network, we found that increasing its ratio from 10% to 20% in the mixture can barely change the curing time. A higher ratio of part B will cause the mixture to be uncurable.

Bonding of PEG Chains onto PDMS Networks. To characterize the bonding between the PEG additive and PDMS after curing, any free PEGMEM that is not reacted with PDMS needs to be removed from the cured PDMS. The PDMS pieces are made very thin (~5 μm thick) by spin-coating the prepolymer mixture onto a clean silicon wafer. Chloroform is a good solvent for PEG and can swell PDMS to a great extent. Soaking cured PDMS pieces in chloroform for a long time can completely extract unreacted PEGMEM from the bulk PDMS. PDMS pieces are characterized after this extraction process.

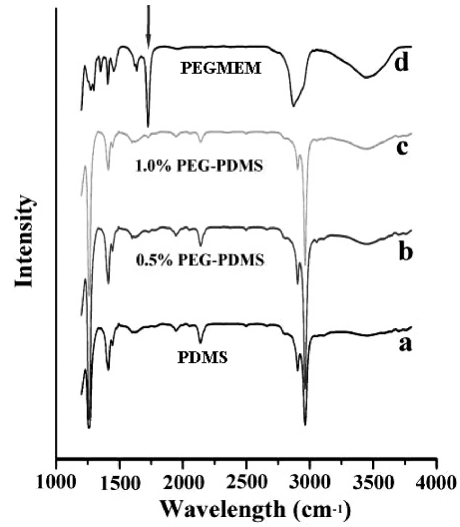


Figure 1. FT-IR spectra of native PDMS (a), PEG modified PDMS [(b) 0.5 wt % PEGMEM and (c) 1.0 wt % PEGMEM] and PEGMEM alone (d).

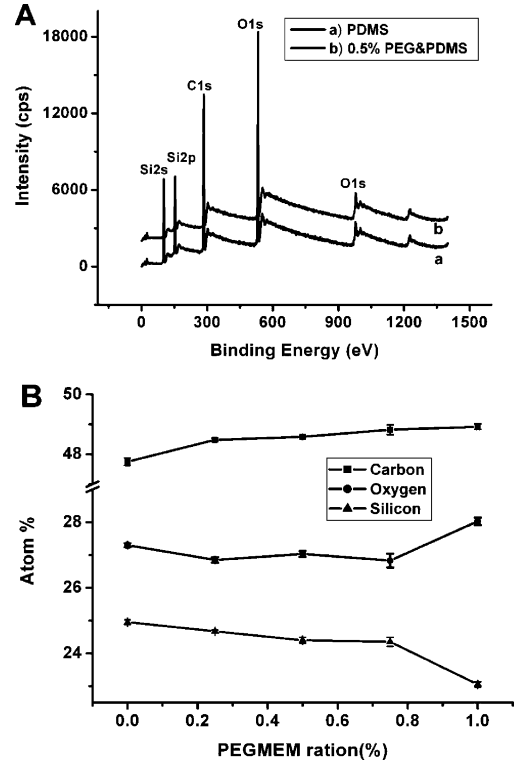


Figure 2. (A) XPS spectra of the surface of native PDMS (a) and 0.5 wt % PEG−PDMS (b). (B) Changes of different element percentages in XPS with the ratio of PEG in PDMS.

Figure 1 shows the FT-IR spectra of PEG−PDMS (0.5 wt % and 1.0 wt % PEGMEM) with the spectra of native PDMS and PEGMEM for reference. The characteristic peak of a carbonyl group (at one end of PEGMEM) at ~1723 cm^{-1} is not shown in the native PDMS spectrum but appears in all other three spectra.[25] The peaks in the PEG-modified PDMS are small because of the tiny amount of PEG in the PEG−PDMS. The broad peak at 3455 cm^{-1} is caused by trace water mainly from PEGMEM. Considering that free PEGMEM has been removed

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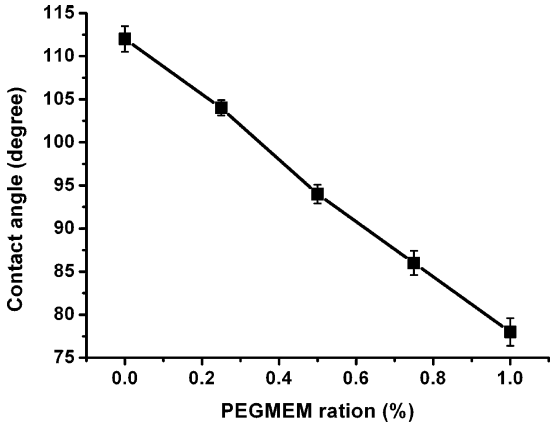

Figure 3. Trend of the contact angle of water on the PEG-modified PDMS surface with different ratios of PEGMEM additive in PDMS.

from the PEG−PDMS, the FT-IR results clearly demonstrate that PEG chains have been linked to the PDMS network.

Surface Characterization of PEG−PDMS Surface. Two independent methods are used to characterize the surface of the PEG-treated PDMS. X-ray photoelectron spectroscopy (XPS) gives the surface elemental composition of PEG−PDMS films, and contact angle measurement shows its hydrophobicity in the macroscopic scale. For both measurements, free PEGMEM is removed from the cured PEG−PDMS piece with chloroform as given above. The XPS spectra of the surfaces of untreated PDMS and PEG−PDMS (Figure 2A) indicate that silicon ratio (atom %) decreases slightly while both carbon and oxygen contents increase slightly when the PEGMEM ratio increases from none to 1.0% (Figure 2B). Although oxygen content may not be a good indicator, because of possible trace oxygen gas and water adsorbed from air, the trends of both silicon and carbon contents qualitatively indicate the existence of PEG on the surface. We also examined the samples after being stored in air at room temperature for 10 days, and the XPS data show the same trend of element content change.

The advancing contact angles at the water/native PDMS interface and water/modified PDMS interface were measured to characterize the wettability of the bulk-modified PDMS. The contact angle of water on the native PDMS surface is 112°. As the content of PEG increases, the contact angle decreases accordingly (see Figure 3). The decrease of the contact angle indicated that the wettability of PDMS increased because of the additive PEG in PDMS. This contact angle shift with the PEGMEM additive ratio further confirms the existence of PEG on the surface. Storage in air at room temperature seems to not change the contact angles significantly.

Resistance against Nonspecific Protein Adsorptions on PEG−PDMS Surfaces. Bovine serum albumin (BSA) represents one of the stickiest proteins. It is commonly used to block nonspecific adsorptions of other active proteins in various surface patterning techniques. We choose BSA as the model protein to examine the capability of the PEG-treated PDMS surfaces for resisting nonspecific protein adsorption.

To compare the amount of protein adsorbed on the surface of PEG−PDMS with a native PDMS surface (as the control), we generated micropatterns of PEG−PDMS on a native PDMS surface with a liquid PDMS transfer technique.[38] A thin layer (~1 μm) of uncured PEG−PDMS liquid was spin-coated onto a flat glass surface (Figure 4A). Part of this thin layer (~0.5 μm) was selectively transferred with the PDMS mold to a flat native PDMS surface. Because only the bottom surface of the PDMS mold was in touch with the uncured PEG−PDMS, a micropattern of PEG−PDMS was generated on the surface of the native PDMS surface after the pattern transfer. After curing, this patterned PDMS was immersed into a fluorescein labeled-BSA solution (5 mg/L in 10 mM phosphate buffer, pH 7.4) for at least 3 h and then washed three times with the phosphate buffer to remove any nonadsorbed protein. Figure 2B shows the fluorescent image of the patterned PDMS after BSA adsorption. The grid and square areas are PDMS and PEG−PDMS surfaces, respectively. The high contrast of fluorescence intensity in the two areas indicates that BSA selectively adsorbs onto the native PDMS surface. By comparing the fluorescent intensity of the two areas, we found that the PEG modification can lower the nonspecific adsorption by ~70%; there is still a significant amount of BSA adsorbing on the PEG-modified surface (0.5 wt % PEGMEM).

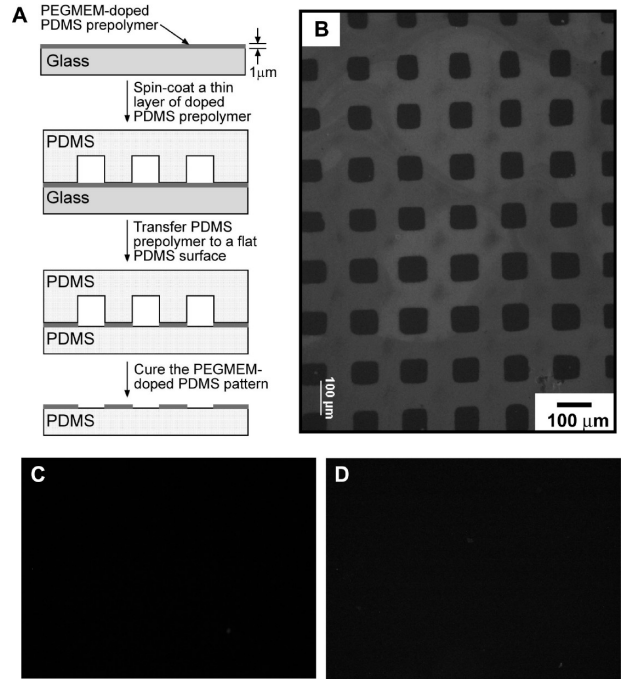

Figure 4. Resistance against nonspecific adsorption of BSA. (A) Process of patterning native PDMS surface with PEGMEM-doped PDMS. (B) Fluorescent image of fluorescein labeled-BSA adsorbed on a patterned PDMS surface (grid area: native PDMS; square area: 0.5% PEG−PDMS). (C) Fluorescent image of 2.0% PEG−PDMS surface after being cured. (D) Fluorescent image of 2.0% PEG−PDMS surface after being immersed into fluorescein labeled-BSA solution and washed thoroughly with phosphate buffer.

To lower the amount of adsorbed BSA, we increase the ratio of PEG in PDMS. Figure 4C,D shows that PDMS with a 2.0% mass ratio of PEGMEM can effectively resist the nonspecific adsorption of BSA. (The fluorescent intensity of the PEG−PDMS surface after the BSA adsorption process is close to that of a background surface.)

CE Separation on PEG-Modified PDMS. We also investigated the application of the PEG-modified PDMS for capillary

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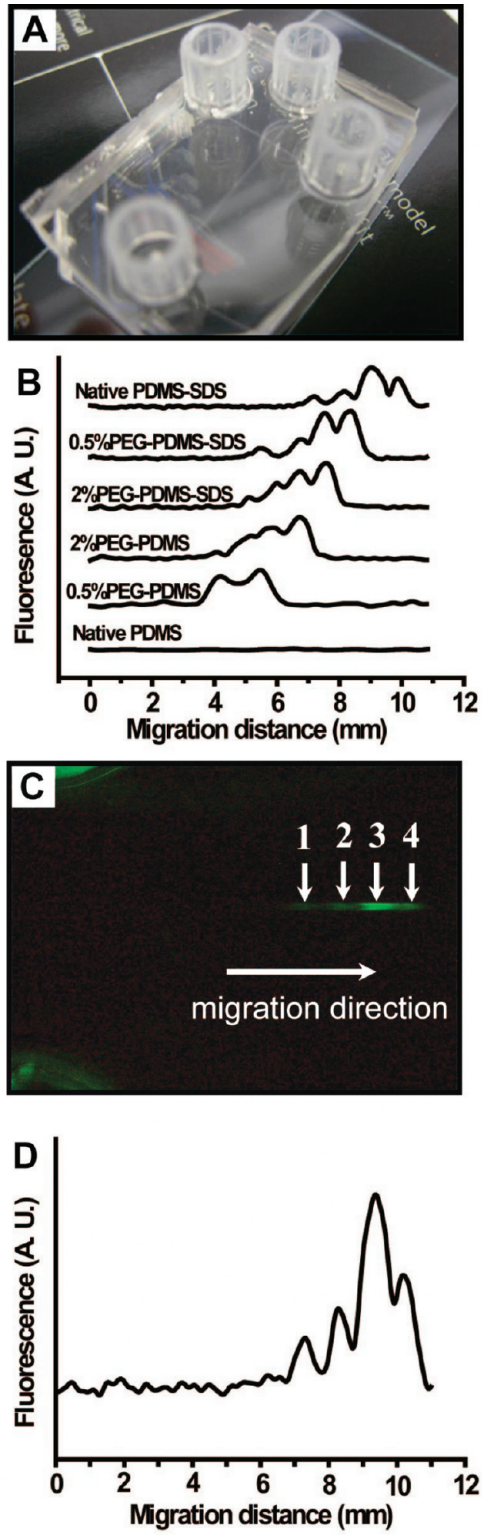

Figure 5. CE separation on PEG−PDMS microchip. (A) Photograph of a CE microchip in 0.5% PEG−PDMS. (B) Electropherograms of FITC-labeled Cyt c, FITC-labeled lysozyme, FITC-labeled lysine, and FITC at 9 s on various chips with or without 0.05% SDS in the running buffer (10 mM phosphate, pH = 7.4). The electropherograms are shifted in the *z* direction for comparison. (C) Video frame of the separation of the four fluorescent molecules at 14 s on the 2.0% PEG−PDMS chip with 0.05% SDS in the running buffer (10 mM phosphate, pH = 7.4). (D) The constructed electropherogram of the separation shown in C. The elution order (from the slowest to the fastest) in all separations is FITC-labeled Cyt c, FITC-labeled lysozyme, FITC-labeled lysine, and FITC.

electrophoresis. Figure 5A shows a CE microchip fabricated with cross microchannels in PEG−PDMS (0.5 wt % PEGMEM and 2.0 wt % PEGMEM). We tested our microchip with a mixture of FITC-labeled Cyt c, FITC-labeled lysozyme, FITC-labeled lysine, and FITC. The separation process was recorded on video with fluorescent microscopy, from which electropherograms are extracted.

Figure 5B gives the electropherograms of these four fluorescent molecules under the voltage of 200 V/cm in microchannels of native PDMS, 0.5 wt % PEG−PDMS and 2.0 wt % PEG−PDMS (with phosphate buffer and sodium dodecyl sulfate (SDS)-containing phosphate buffer, pH = 7.4 in both buffers), respectively. The fluorescent video images of each separation at 9 s after the "pinch" injection on different chips are exacted and used to construct the electropherograms. No fluorescent signal can be observed in the native PDMS microchips without SDS in the buffer because of the lack of EOF. The PEG−PDMS microchips under the same separation conditions show improved separations with peaks unresolved. We believe that a relatively more hydrophilic PEG−PDMS surface can attract some charges and support weak EOF. Doping a minute amount (0.05%) of SDS in the separation buffer can cause successful CE separations in both native PDMS and PEG−PDMS channels at 9 s. It is also clearly seen that, with SDS in the separation buffer, the EOF in the native PDMS channel is much stronger (running faster) than that in the PEG−PDMS channel. Because the chip has a separation channel with ~1.8 cm, the analytes will migrate into the outlet reservoir with a longer separation time in the native PDMS chip (with SDS-doped buffer). A longer separation time at 14 s on the 0.5% PEG−PDMS chip (with SDS-doped buffer) cause more effective separation (Figure 5C,D).

Although it is clear about the relative strength of EOF in different situations from the electropherograms in Figure 5B, measurement of EOF can give the accurate information about surface charge density. We adopted the current-monitoring method that was established by Huang et al.[39] to measure the EOF quantitatively. In the 10 mM phosphate buffer (pH = 7.4), the EOFs of the native PDMS, 0.5 wt % PEG−PDMS and 2.0% PEG−PDMS microchips are 2.54×10^{-4} cm^2/V/s, 3.12×10^{-4} cm^2/V/s, and 3.65×10^{-4} cm^2/V/s, respectively. When 0.05% SDS was added, the EOFs of these three surfaces are changed to 5.43×10^{-4} cm^2/V/s, 4.51×10^{-4} cm^2/V/s, and 4.18×10^{-4} cm^2/V/s, respectively. When stored in the SDS-doped buffer for ~10 days, the EOF of the PEG−PDMS can decrease slightly (~10%). The results indicate that SDS can adsorb to all these surfaces and enhance their EOF with native PDMS having the largest enhancement. According to previous studies,[11] the hydrophobic tail of SDS molecules can adsorb to the hydrophobic surface and present the negatively charged sulfate group to buffer and enhance EOF. Apparently, native PDMS has the entire surface for SDS adsorption; increasing the amount of PEG will reduce the hydrophobicity available for SDS adsorption, thus lowering the EOF enhancement. The EOF measurements suggest that PEG domains exist on the PEG−SDS surface and the coverage of these domains increases with the ratio of PEG in the material. Others also found

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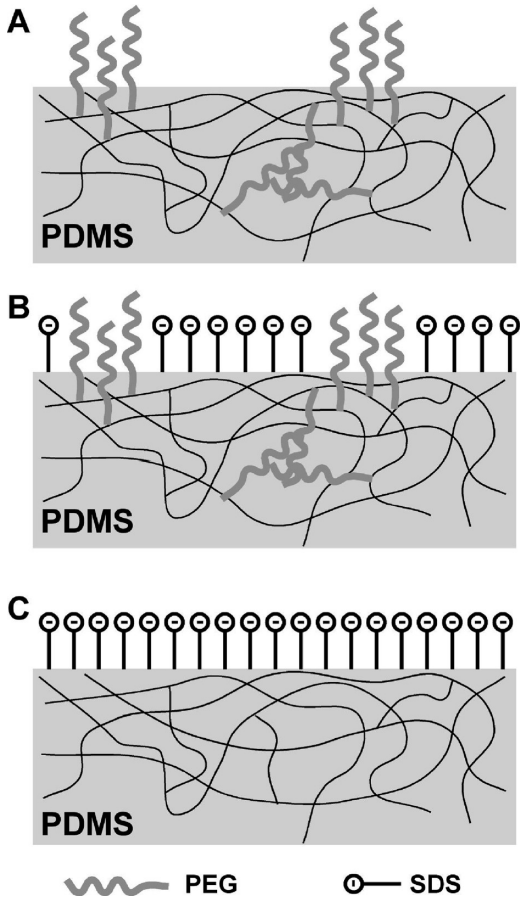

Figure 6. Inference of molecular arrangements on the surface of (A) PEG−PDMS, (B) PEG−PDMS in SDS-containing buffer, and (C) native PDMS in SDS-containing buffer.

that nanodomains of PEG commonly exist on the surface of PEG−SDS diblock copolymers.[40]

Inference of Molecular Arrangements on PDMS Surfaces. On the basis of our results, we give a schematic illustration of the molecular arrangements on the PDMS surfaces (Figure 6). Both in the bulk and at the surface of a PEG-modified PDMS (Figure 6A), the cross-linked PEG chains will have a phase separation from PDMS and form PEG nanodomains[40] because of their poor compatibility with PDMS network. Our results show that small amount (2.0 wt %) of PEGMEM can greatly resist nonspecific protein adsorption. Possible reasons for this effectiveness can be (1) during the curing process of PDMS, some PEGMEM molecules (relatively long molecule with ~10 ethylene oxide units) migrate to the surface, causing a relatively higher PEGMEM ratio on the surface, and (2) surfaces with nanodomains of PEG/PDMS are not favorable for protein nonspecific adsorption. A low PEGMEM ratio reduces the capability of resisting nonspecific protein adsorptions because the PEG chain on the surface is not enough to cover the entire PDMS surface; in this case, SDS surfactant molecules in buffer solution can adsorb onto the exposed (uncovered by PEG), hydrophobic PDMS surface (Figure 6B).[13] These adsorbed SDS molecules give moderate EOF for successful CE separations. In contrast, all surface area on the surface of a native PDMS microchannel is covered by SDS molecules, which provides very strong EOF (Figure 6C).

(40) Fang, H. X.; Zhou, S. X.; Wu, L. M. *Appl. Surf. Sci.* **2006**, *253*, 2978–2983.

CONCLUSIONS

This report describes a simple, fast, and reproducible method for the modification of a PDMS surface with PEG chains to resist nonspecific protein absorption. A small amount of PEG molecules terminated with a vinyl group that are added into the PDMS prepolymer will be covalently linked to the PDMS network simultaneously when the PDMS is thermally cured. Compared with other methods, this method is far more convenient without multiple steps and organic solvents. Schematic illustrations are also given to successfully explain the surface properties of the modified PDMS surfaces. Other types of molecules with a similar structure could also be covalently incorporated into the PDMS network with the same procedure. We believe that this method of modifying PDMS and the PEG-ylated PDMS will be useful in fields including microfluidics and bioengineering.

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