Formation and Properties of Responsive Siloxane-Based Polymeric Surfaces with Tunable Surface Reconstruction Kinetics

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Here, the formation of responsive polymeric materials with tunable response time is reported. These structures are fabricated by chemically modifying poly(vinylmethyl siloxane) (PVMS) networks with alkanethiols bearing a hydrophilic end-group ($-\text{COOH}$ or $-\text{OH}$). The response time is facilitated by the liquid nature of the PVMS backbone and increases with increase in length of the methylene spacer $(-\text{CH}_2)_n-$ in the alkanethiol pendent group. While for $n = 2$ and 6 , the surface reconstructs almost instantaneously, specimens with $n = 11$ resist reconstruction because of strong van der Waals forces, leading to the formation of semi-crystalline regions. It is demonstrated that the responsive nature of $\text{PVMS-S}-(\text{CH}_2)_{11}\text{OH}$ can be fine-tuned by varying the temperature; it possesses a faster response at temperatures above the melting point of the $-\text{S}-(\text{CH}_2)_{11}\text{OH}$ moiety.

“ultimate” responsive surface is one that instantaneously responds to changes in its environment with a measurable property change. Defining the optimum response of a switchable surface involves understanding the characteristics responsible for the change in surface properties. Creating a surface that turns on or off within an optimum timeframe first requires a measurable magnitude change in response to environmental changes such as temperature, pH, or chemical composition. In addition, the reversibility of a true switchable surface should not deteriorate over time.

Polymers offer a convenient material platform for generating responsive surfaces. The mobility of the backbone (and hence the response time) can be adjusted by varying the application temperature relative to the polymer's glass transition temperature, T_g . Additional tunability can be achieved by confinement; recent results have shown that the T_g is lower in the surface region than in the bulk enhancing surface reconstruction rates.^[8–10] In addition, polymers can be readily chemically functionalized, which could encompass attaching hydrophobic, hydrophilic, or specific recognition receptor moieties. Overall, it is the combination of the solid–liquid duality due to T_g and local molecular heterogeneities along the polymer backbone that provide convenient means of tuning the response time of polymeric materials to changes in the environment.

The dynamic nature of polymer surfaces, reconstruction dynamics associated with switching the external medium, and changing the chemical make-up of the surface itself has been studied by several research groups in the past. Early on, Whitesides and coworkers evaluated the wettability of oxidized polyethylene after various environmental exposures and temperature variations.^[11] Koberstein reported on the responsiveness of synthetic polymeric systems equipped with various end-groups ranging from hydrophilic (i.e., carboxylic acid) to hydrophobic (i.e., various fluorine-containing moieties).^[12] By varying substrate elasticity and composition of oxidized butadienes to create a system with a controlled rate of surface reconstruction, Ferguson and coworkers argued that surface reconstruction was dictated by shifts in enthalpic and entropic driving forces on the surface free energy.^[13–15]

Surface reconstruction is also associated with surface segregation of polymers and their reorientation at the surface.

1. Introduction

A responsive surface adapts its physico-chemical characteristics in response to an external stimulus, be it chemical, electrical, or mechanical.^[1–6] It can entail a recognition event that triggers a conditional response. Consider, for instance, a pH-responsive polymer conjugated with glucose oxidase and embedded with insulin. When sufficient levels of glucose are present in the contacting media, a decrease in the pH causes a matrix pore-size change due to polymer collapse, thereby releasing insulin.^[7] Such materials are often described as biomimetic^[4] due to their ability to mimic the efficient conversion of chemical energy into mechanical energy in living organisms and their use has been demonstrated in artificial muscles.^[7] In many cases, surface responsiveness results from the rearrangement of various chemical functionalities present close to or directly at the surface. The two key parameters that define the functionality (and ultimately application) of any responsive surface are i) the degree of change of the surface properties after the external trigger was applied and ii) the rate at which these variations occur. Hence an

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These two modes often act in accord and contribute simultaneously to variations in surface activity. First, polymer mobility in the bulk and at the surface depends on system temperature. While polymer motion in a glassy state is very slow, it increases dramatically when the temperature of the system is raised above T_g . At temperatures above T_g the polymer chains can restore their preferred random flight conformations if an entropic gain exceeds enthalpic interactions between the polymer and the surface, unless there is an additional constraint, such as the presence of crystalline or cross-linked regions. There are applications where surface stability is desired. For instance, Genzer and Efimenko implemented a mechanically assisted monolayers (MAMs) technique to manipulate the packing density of hydrophobic molecules attached chemically to poly(dimethyl siloxane) (PDMS) networks hydrophilicized with a brief exposure to ultraviolet/ozone treatment.^[16] By performing the surface modification under strained conditions, fluorinated alkane silanes had sufficient space to orient perpendicular to the surface. Upon release of the strain, these molecules were “squeezed” into a dense alignment preventing chain reorientation. Rouse et al.’s work on “frustrated” glassy surfaces also accentuated entropic control at a polymer interface by manipulating the reconstruction temperature.^[17] Using poly(4-methyl styrene) as a model glassy polymer, Rouse et al. oxidized its surface below the polymer’s T_g of 110 °C. The resulting functionalized surface was “locked” and remained hydrophilic when exposed to air below its bulk T_g .

A direct correlation exists between polymer elasticity and surface response. Starting with a very flexible substrate, such as a silicone elastomer, one increases the likelihood of generating prompt responses to external stimuli. Relatively inert PDMS does not lend itself to a dual-characteristic surface. However, replacing one of the methyl groups in PDMS with another chemical moiety, such as vinyl in the case of poly(vinylmethyl siloxane) (PVMS), increases chemical tailorability. PVMS is a unique polymer providing multiple functions: i) the low surface energy methyl group, ii) the highly flexible siloxane backbone, and iii) the vinyl moiety that can be used as an attachment point for various chemistries. We incorporated this design flexibility into our research by i) synthesizing various molecular weight PVMS with reactive end-groups for subsequent network formation, ii) utilizing alkoxy-condensation cure chemistry for network formation that would allow us to later react the vinyl moieties, and iii) modifying PVMS with hydrophilic and hydrophobic functionalities.

Our initial observations of reversible PVMS siloxane surfaces was demonstrated with deionized (DI) water contact angle (θ_{DIW}) measurements.^[18] As the vinyl group has a slightly higher surface energy than the methyl group, it hides beneath the surface when exposed to hydrophobic environments, such as air. Exposure to water leads to a rearrangement of the surface moiety makeup as the preferred state is orientation of the vinyl groups at the surface. As contact angle measurements are sensitive to just the first ~5 Å of the polymer surface,^[19] the composition rearrangement can be observed by time-dependent contact angle measurements and utilized to characterize response kinetics of modified and unmodified PDMS and PVMS surfaces. We have shown previously^[20] that the rate of change of contact angle with time ($d\theta_{DIW}/dt$) of water exposure time was found to be constant for

PDMS networks. In contrast, the PVMS data indicated the existence of two wettability regions: i) as water comes into contact with the PVMS surface, the system minimizes its free energy by replacing the hydrophobic methyl groups with higher-surface energy vinyl moieties at the PVMS/water interface and ii) the rapid decrease in the contact angle recorded at the short exposure times can thus be associated with the aforementioned rearrangements of the functionalities on the surface. While the rapid rate of the PVMS response is a consequence of the high flexibility of the Si–O backbone, the surface energy difference between the methyl and vinyl substituents is small. To further accentuate the difference in surface energy effects, we modified the vinyl moiety on the PVMS substrate through a thiolene addition reaction.^[21] Utilizing this surface modification technique enables the introduction of siloxane networks as a novel platform of substrates capable of rapidly reorganizing in the presence of polar media.

In this paper, we build on the responsive nature of PVMS surfaces by grafting amphiphilic moieties on the silicone elastomer backbone. Specifically, we provide evidence that the combination of the high flexibility of the silicone elastomer chain and the amphiphilic nature of the side groups endows these materials with exceptionally fast surface reconstruction kinetics and a high degree of repeatability. Moreover, we show that additional control over the molecular arrangement on such substrates can be achieved when the amphiphilic moieties attached to the PVMS backbone can locally crystallize.

2. Results and Discussion

2.1. Modified PVMS Surfaces

Implementing the thiol-ene addition reaction on PVMS networks, a route others demonstrated with fluid polymers,^[15,22–24] we modified PVMS substrates with 11-dodecanethiol ($\text{HS}(\text{CH}_2)_{11}\text{CH}_3$) and 3-mercaptopropionic acid ($\text{HS}(\text{CH}_2)_2\text{COOH}$). The addition to the vinyl bond was confirmed via the elimination of the C=C peaks at 960, 1407, and 1587 cm^{-1} in Fourier transform infrared spectroscopy in the attenuated total reflection mode (FTIR-ATR). In Figure 1, we plot the FTIR-ATR data for the 11-dodecanethiol addition to PVMS. The results indicate a high yield of attachment of the alkane groups; the peaks corresponding to the vinyl group in the modified samples were absent after the thiol-ene reaction. The surface composition variation in thiol-ene modified-PVMS samples was also confirmed by a change in the water contact angle. The dodecane group is more hydrophobic than the methyl group, as is apparent in the water contact angle shift of ~105° before modification to ~125° after modification (Fig. 1). Note that the thiol-ene reaction with 11-dodecanethiol took place in the bulk siloxane fluid. This modified PVMS fluid was subsequently crosslinked through its hydroxyl endgroups. The high water contact angle (~125°) of the PVMS–S– $(\text{CH}_2)_{11}\text{CH}_3$ substrate is likely due to both the hydrophobicity of 11-dodecanethiol and the inherent roughness of cross-linking such a heavy substituted siloxane chain.

Obtaining dual-responsiveness of the opposing substituent groups requires a situation as illustrated in Figure 2 for the

Figure 1. FTIR-ATR spectra of bare PVMS (dashed line) and PVMS after thiol-ene addition of 1-dodecanethiol, PVMS-S-(CH₂)₁₁CH₃ (solid line). The PVMS network was prepared by crosslinking PVMS chains ($M_n = 39$ kDa) with a 70% excess of TEOS cross-linker. Vinyl peaks at 960, 1407, and 1587 cm⁻¹ in the thiol-ene modified sample are not present. The inset shows photographs of water droplets on PVMS and PVMS-S-(CH₂)₁₁CH₃ samples.

carboxy- and alkyl-functionalized siloxane substrates. When the surface is exposed to air, the methyl groups populate the substrate/air interface while the carboxy-terminated pendent group resides underneath the surface. Exposing the substrate to water repels the methyl groups from the surface and attracts the carboxy-groups in their stead to maximize the polar interactions. The opposite situation is expected for alkyl-terminated PVMS.

Figure 2. Schematic illustrating the molecular orientation of PVMS modified with 3-mercaptopropionic acid (HS(CH₂)₂COOH) and 11-dodecanethiol (HS(CH₂)₁₁CH₃) at the air/sample and water/sample interfaces.

Figure 3. Time-dependent water contact data for PVMS substrates ($M_n = 39$ kDa, $R = 1.7$ moles of cross-linker/moles of polymer): bare PVMS (■), PVMS-S-(CH₂)₁₁CH₃ (▲), and PVMS-S-(CH₂)₂COOH (◆). Average error in contact angle measurement is $\pm 1.5^\circ$.

Here alkyls longer than methyl are expected to populate the substrate/air interface but will “hide” beneath the surface when exposed to water, thus allowing the shorter and less hydrophobic methyls to occupy the sample surface. To confirm that the thiol-ene addition modification resulted in a dual-energy surface, time-dependent water contact angle measurements were performed at room temperature for PVMS, PVMS-S-(CH₂)₁₁CH₃, and PVMS-S-(CH₂)₂COOH, as demonstrated in Figure 3. After three minutes of exposure to the probing water droplet, the PVMS-S-(CH₂)₁₁CH₃ substrate became less hydrophobic; the contact angle changed from ~ 125 to $\sim 115^\circ$. In contrast, the high energy PVMS-S-(CH₂)₂COOH substrate responded almost instantaneously to water exposure with a 2° per second drop in contact angle. This ultrafast response has been attributed to both the high flexibility of the polymer backbone and the large chemical disparity between the methyl and carboxylic acid groups.

Surfaces with fast and reversible reconstruction are needed for designing materials with real-time switchable behavior. Other researchers observed that reversibility disappeared after several switching cycles.^[14,25–27] In order to return the material to the original surface composition, another stimulus, such as temperature, had to be applied.^[11] We postulated that, as barriers to rotation for the siloxane backbone are very low, the PVMS network would easily reorient in a new media to favor the lowest energy state. We observed this behavior during a reversibility study with the PVMS-S-(CH₂)₂COOH surface in contact with the water droplet (Fig. 4). After the first cycle of rapid surface reorientation, we removed the water droplet via adsorption by a Kim wipe. The surface was dried with a stream of nitrogen and allowed to rest in ambient conditions for 3–5 min. At this point, we applied another water droplet to the same location on the surface. Excellent reversibility was observed (Fig. 4) as the surface was able to return to its original hydrophobic state, indicating that: i) residual water was removed from the surface, as contact angles exceeding 110° would be difficult to obtain otherwise, ii) the -S-(CH₂)₂COOH moieties easily reoriented beneath the

Figure 4. Ability of PVMS-S-(CH₂)₂COOH to reverse its wettability behavior. The inset shows schematically the conformation of the -S-(CH₂)₂COOH linker in response to the variation of the environment.

surface upon removal of the water drop, and iii) returned to the surface when exposed to additional water. The data in Figure 4 indicate that the reversible behavior may be dampening, as the third cycle's starting contact angle was 1–2° less and ended with the lowest contact angle of the three sets (~55°).

It is instructive to compare the reorientation kinetics detected in our PVMS-based materials to that reported previously for other systems. For example, oxidized polyethylene reoriented only at elevated temperatures due to its high T_g .^[11] While it restructured to its hydrophobic state in vacuum at 100 °C within a few minutes, our PVMS-S-(CH₂)₂COOH responded in seconds at room temperature.^[28] Fluorine-terminated polystyrene exposed to a saturated humid environment decreased 10° in water contact angle after ten days of contact time.^[29] The surface segregation of polyisoprene in PS-*b*-PI-(CH₂)₃N(CH₃)₂ occurred after annealing the surface for 24 h at 170° (above the T_g) and the dimethylamine end group reoriented only after 6–10 days of humidity exposure.^[30] Oxidized 1,2-polybutadiene took hours to oscillate between hydrophobic and hydrophilic surfaces when relying solely on contacting media effects at room temperature but did respond within minutes to heated water.^[15] To our knowledge, the observed reorientation kinetics of PVMS-S-(CH₂)₂COOH thus possesses the fastest responses ever reported for any polymeric surface.

2.2. Tailored Wettability Switching Kinetics and Reconstruction Reversibility

Inspection of the data for the PVMS-S-(CH₂)₁₁CH₃ substrate in Figure 3 indicates its loss of hydrophobicity after exposure to water, as the methyl groups have a higher surface energy compared to the 11-dodecanethiol substituents. While the surface reconstruction occurs, it does so at a slower rate than for the PVMS-S-(CH₂)₂COOH substrate. This behavior can be attributed to the difference in the methylene spacers where a -(CH₂)₁₁-spacer would be more “sluggish” to rearrange than a shorter

-(CH₂)₂- spacer. In order to comprehend the mechanism of surface rearrangement, we chemically grafted mercaptoalkanols with methylene spacers with a variable length.^[21] Evaluating the surface response of mercaptoalkanols versus mercaptoalkanoic acids eliminated any possible complications of acid–base interactions due to the carboxy groups.^[11,31,32] As previously, we study the surface rearrangement kinetics by monitoring wettability changes using static contact angle measurements. To further characterize surface reconstruction in the mercaptoalkanol-modified PVMS substrates, we exposed the specimens to alternating wet and dry cycles utilizing dynamic contact-angle measurements to study hysteresis in the surface reorganization. We will demonstrate that an increase in the number of methylene spacers in the mercaptoalkanols leads to slower reorganization kinetics and eventual loss of surface switching due to the tendency of these side groups to form semi-crystalline domains at the surface.^[33–35]

PVMS sheets were modified with three different mercaptoalkanols: HS(CH₂)₂OH, HS(CH₂)₆OH, and HS(CH₂)₁₁OH. In Figure 5 we compare the static contact angle of DI water (θ_{DIW}) as a function of time for each mercaptoalkanol-modified PVMS surface. PVMS-S-(CH₂)₂OH exhibited a very fast drop in contact angle upon exposure to water ($\Delta\theta_{DIW} \approx 35^\circ$). In contrast, PVMS-S-(CH₂)₁₁OH revealed only a modest change in contact

Figure 5. Time dependence of the DI water wettabilities for PVMS-S-(CH₂)_nOH surfaces. The error for θ_{DIW} is $\pm 1.5^\circ$. The lines represent the best fits to $-\cos(\theta_{DIW}) = A + B e^{-Ct}$, where t is time in seconds. The values of A, B, and C are: $n=2$: $A=-0.255$, $B=0.597$, $C=-0.0375$; $n=6$: $A=-0.190$, $B=0.387$, $C=-0.0355$; and $n=11$: $A=-0.198$, $B=0.162$, $C=-0.0055$.

angle ($\Delta\theta_{\text{DIW}} \approx 7^\circ$). This rather sluggish response of PVMS-S-(CH₂)₁₁OH upon exposure to water is attributed to a reduced mobility of surface-bound -(CH₂)₁₁- side chains due to characteristic semi-crystalline behavior. As we will demonstrate later, this behavior is inferred from a transition from a transparent to an opaque state, $\sim$ ten-fold increase in the storage modulus, differential scanning calorimetry (DSC), and a transition from a liquid-like to a semi-crystalline-like state established by infrared spectroscopy.

While the PVMS-S-(CH₂)₂OH and PVMS-S-(CH₂)₆OH surfaces initially displayed fast surface reorientation kinetics after water exposure, it is the repeatability of the cycling behavior between wet and dry states that critically determines the viability of these surfaces as stimuli-responsive materials. In order to evaluate wettability cycling with minimal sample handling we utilized a Cahn dynamic contact analyzer (DCA) using methodology described in the Experimental section. Figure 6 depicts cycling wettabilities measured for unmodified PVMS and PVMS-S-(CH₂)_nOH; one cycle represents an average of all measurements carried out on three separate specimens. For PVMS, the repeated oscillations displayed only minute changes in surface wettability, in agreement with previous findings.^[20,21,28] For PVMS-S-(CH₂)₂OH and PVMS-S-(CH₂)₆OH, the repeated DCA oscillations demonstrated a close compliance with the static contact angle results. The difference between contact angles of the dry and wet states for PVMS-S-(CH₂)₆OH was consistent through all cycles with only a slight decrease in starting contact angle. PVMS-S-(CH₂)₂OH cycles were even more repeatable with little sign of any dampening behavior. This substrate exhibited the largest change in contact angle and

displayed a greater starting hydrophobic value after the initial cycle. Since this chain possessed the shortest methylene linker, the flexibility of the siloxane backbone remained intact, thus allowing for the restructuring to occur very rapidly between the methyl and 3-mercaptopropanol substituents. The behavior of PVMS-S-(CH₂)₁₁OH was more complex, however. While we observed an initial surface reorientation after the first water-dipping cycle, the surface “froze” in the hydrophobic state during all subsequent cycles. We attempted to recover the original hydrophilic response of PVMS-S-(CH₂)₁₁OH by exposing the specimens to hot water (95 °C) for 60 min. After the heat-treatment, the surface reorientation was frozen by immersion in 25 °C water and dried with nitrogen. This surface reoriented to a stable, more hydrophilic surface ($\theta \approx 80^\circ$). Continued monitoring of the specimen revealed a slow reconstruction to the hydrophobic state ($\theta \approx 96^\circ$) after exposure to air for several days. We note that it was possible to quickly restructure the surface to a starting contact angle of $\sim 105^\circ$ if the sample was heated in water and allowed to slowly air cool versus quenching in 25 °C water. This result is consistent with the findings of Carey et al.^[13] and Holmes-Farley et al.^[11] for surface restructuring of oxidized polybutadiene and oxidized polyethylene, respectively.

Further information pertaining to chain reorganization on the PVMS surfaces was gathered from monitoring the contact angle hysteresis with the DCA experiments. During the immersion and emersion stages, the advancing and receding contact angles were measured as a function of the exposed substrate. Contact angle hysteresis, defined here as $\theta_{\text{advancing}} - \theta_{\text{receding}}$ ($\Delta\theta$), is a measure of several factors, including surface roughness, surface homogeneity, sample swelling or liquid penetration, and surface reorientation.^[36] As we are maximizing surface mobility with the siloxane backbone, surface reorientation and heterogeneity would be the likely contributors to contact angle hysteresis. Figure 7 depicts the $\Delta\theta$ for PVMS and the three mercaptoalkanol-modified substrates over the ten cycles. The most responsive surface, PVMS-S-(CH₂)₂OH, has the largest observed hysteresis of $\sim 75^\circ$, consistent with its repeatable and reversible state between a polar and nonpolar environment. Besides PVMS,

Figure 6. Time dependence of the DI water wettabilities for PVMS-S-(CH₂)_nOH surfaces measured by dynamic contact angle. The error for θ_{DIW} is $\pm 1.5^\circ$.

Figure 7. Contact angle hysteresis ($\Delta\theta = \theta_{\text{advancing}} - \theta_{\text{receding}}$) for a dynamic contact angle cycle depicted in Figure 5 for: PVMS (■), PVMS-S-(CH₂)₂OH (●), PVMS-S-(CH₂)₆OH (▲), and PVMS-S-(CH₂)₁₁OH (◆).

PVMS-S-(CH₂)₁₁OH has the smallest hysteresis, continually decreasing with each wet/dry oscillation. This observation is consistent with the notion that we had formed a stable surface in this sample by inducing crystallinity. In the following section, we provide more detailed picture of how chain crystallinity observed in the PVMS-S-(CH₂)₁₁OH samples influences chain dynamics on PVMS surfaces.

2.3. Determination of Semi-Crystallinity

In addition to the aforementioned differences in wettabilities, we observed visual changes among the samples. Specifically, the PVMS, PVMS-S-(CH₂)₂OH, and PVMS-S-(CH₂)₆OH specimens were transparent, elastic and tacky; they adhered well to a polystyrene Petri dish. In contrast, the PVMS-S-(CH₂)₁₁OH materials were opaque, rigid, and nonadhering to polystyrene (Fig. 8). Upon immersion into hot water (temperature ≥ 70 °C), however, PVMS-S-(CH₂)₁₁OH became transparent but turned opaque again upon cooling. The loss of transparency is a classical indicator of semi-crystalline behavior as crystallites impede light propagation through the material.

The opaqueness indicator for the formation of crystalline domains with the -S-(CH₂)₁₁OH modification was also confirmed with optical microscopy at both room temperature and elevated temperature. Specifically, PVMS-S-(CH₂)₁₁OH was placed over a transparent printout bearing a sign "NCSU" on a heating stage under the microscope. Heating at a rate of 1 °C per minute, images (5 $\times$ magnification) were acquired every 30 s to track the melting temperature transition. Inspection of the images (Fig. 9) indicated this transition occurred between 28 and 32 °C. At elevated temperatures (>45 °C) the letters were clearly visible under the microscope. Upon lowering the temperature, the "NCSU" sign became illegible and almost completely blocked

Figure 8. Photographs of mercaptoalkanol-modified PVMS substrates in front of an opaque background; ① PVMS ② PVMS-S-(CH₂)₆OH and ③ PVMS-S-(CH₂)₁₁OH. The opaqueness of ③ is indicative of crystallites.

Figure 9. A sample of PVMS-S-(CH₂)₁₁OH observed with optical microscopy (at 5 $\times$ and in reflectance mode).

at temperatures below 32 °C. This experiment was conducted only for illustrative purposes rather than aimed at pinpointing the exact transition temperature. In addition, while the hot stage used for the temperature ramp had poor control below 30 °C, it still demonstrated the substrate's ability to oscillate between either an opaque or transparent state.

In addition to the visual observations, additional experiments were performed on PVMS and the modified substrates^[37] to further quantify the temperature transitions including dynamic rheology, DSC, and FTIR-ATR studies. As noted above, it was obvious through sample handling that the PVMS-S-(CH₂)₁₁OH substrate was more rigid than the other modified samples. This observation was further confirmed via dynamic rheology experiments that revealed a ten-fold increase in the storage modulus G' (Fig. 10). Although the modulus did increase, the G' data for PVMS-S-(CH₂)₁₁OH is frequency-dependent, indicating an imperfect network (frequency sweep was performed within the linear viscoelastic regime at 0.5% strain). In contrast, PVMS, PVMS-S-(CH₂)₂OH, and PVMS-S-(CH₂)₆OH are considered to be nearly perfectly elastic as a zero slope was obtained for the G' versus frequency sweeps, as documented by data shown in Figure 10a. Upon heating semi-crystalline material, ordered polymer chains will relax into their preferred random coil conformations above a melting transition. To determine if this held true for the PVMS-S-(CH₂)₁₁OH substrate, more detailed analysis of the rheological properties was performed by varying the run temperature for the dynamic frequency sweep tests as shown in Figure 10b and c. At an operating temperature of 50 °C, the melting transition (melting point of 11-mercaptoundecanol is between 33 and 37 °C)^[38] had been reached in the data in Figure 10b as this temperature-induced polymer relaxation state resulted in negligible frequency dependency. This indicated the PVMS-S-(CH₂)₁₁OH network had reached near-perfect elasticity. Figure 10c illustrates that upon cooling there is full network recovery as this data replicates those obtained during the run before heating. It thus appears that the ordered alkane chains are

Figure 10. Dynamic rheology on PVMS and mercaptoalkanol-modified PVMS substrates. Runs performed at sequential operational temperatures (T): a) $T = 23$ °C, b) $T = 50$ °C, and c) $T = 23$ °C. The average standard deviation of data is ± 33 kPa.

acting as filler-like reinforcers at room temperature, disrupting the elastic nature of the siloxane network.

The T_g is largely due to the intramolecular interactions within the backbone, polarity of the substituents, backbone flexibility, and barriers to rotation. As the bulkiness of the substituents increases, a rise in T_g is typically apparent. The T_g rose remarkably in all three modified samples corresponding to other siloxane polymers that have substituent markedly different from the methyl group as quantified by dynamic scanning calorimetry (Fig. 11). Our modified substrates exhibited an increase in both the chain length and polarity of the silicon vinyl substituent contributing to the higher temperature transitions in comparison to PVMS. Furthermore, the temperature profile for PVMS-S-(CH₂)₁₁OH was different than its liquid-like counterparts as a melting transition exists as evident by the distinct endothermic peak of this scan. More detailed analysis of the effect of molecular structure of PVMS and thiol-modified PVMS substrates on T_g and T_m will be presented in a future publication.^[39]

FTIR-ATR spectroscopy further supported our claim that the 11-mercapto-1-undecanol-modified PVMS surface had undergone a phase transition with the formation of semi-crystalline domains. The data in Figure 12 depict the decrease in frequency shift for both asymmetric and symmetric C-H stretches of the methylene group. The characteristic frequency for the C-H

Figure 11. DSC for PVMS and PVMS-modified substrates. The heating rate was 3 °C min⁻¹, see text for details.

Figure 12. ATR-FTIR data within the methylene stretching region for PVMS and the mercaptoalkanol-modified samples. The resultant chromatogram for each specimen was deconvoluted with multi-peak Gaussian fits using OriginLab. The higher wavenumber peak is the characteristic asymmetric methylene stretching vibrations and the lower wavenumber is the characteristic symmetric methylene stretching vibrations. As crystallinity increases, the frequency vibrations shift to lower wavenumbers.

stretching vibrations (asymmetric) occurs at 2920 cm⁻¹ for crystalline polymethylene chains. For the liquid polymethylene state, the C-H stretching vibrations (asymmetric) are detected at 2928 cm⁻¹.^[35] A similar downward shift for the symmetrical C-H stretching vibrations is observed for liquid (2856 cm⁻¹) to crystalline (2850 cm⁻¹) transition of the polymethylene chain.^[35] Our results for the modified PVMS substrates reveal that while the -S-(CH₂)₆OH substituted surface is in a liquid-like state, the -S-(CH₂)₁₁OH group is in a crystalline-like state. Our observed frequency shifts between these two substrates agree closely with the reported polymethylene transition. Our results are also in accord with those of Chaudhury and Owen,^[34] who showed that adhesion hysteresis can be tuned by varying the surface density of hexadecyltrichlorosilane (HTS) chemisorbed films on PDMS. Highly packed films of HTS were found to be crystalline ($\nu_a(\text{CH}_2) = 2919 \text{ cm}^{-1}$ and $\nu_s(\text{CH}_2) = 2850 \text{ cm}^{-1}$) with high adhesion hysteresis. The opposite was true for a less dense film of HTS. From all the evidence presented, we infer that after the first wet-dry cycle, -S-(CH₂)₁₁OH groups were trapped just beneath the surface in a semi-crystalline structure, formed presumably via van der Waals interactions acting among

Figure 13. ATR-FTIR data recorded within temperature range of 23–55 °C for PVMS-S-(CH₂)₁₁OH. As the temperature increases the material transitions through a melting region and loses some crystallinity. This is reflected in an upward frequency shift for the characteristic asymmetric and symmetric methylene stretching vibrations with increasing temperature (see inset). The light and dark lines represent the measurements below and above the melting temperature (T_m) of HS-(CH₂)₁₁OH, respectively ($T_m = 35$ °C).

neighboring -(CH₂)₁₁- chains, and did not respond to the presence of water on the surface. Annealing the sample appeared to partially “melt” the semi-crystalline regions as the substrate became transparent, hence allowing the mercaptododecanol side-chains to reconstruct moderately at the surface.

As we detected the melting transition for PVMS-S-(CH₂)₁₁OH both visually and with dynamic rheology, we expected that FTIR-ATR studies performed at elevated temperatures would result in C-H stretching vibrations characteristic of a liquid-like state. The data in Figure 13 illustrate this behavior. We heated PVMS-S-(CH₂)₁₁OH from room temperature to 55 °C. At each step interval, the temperature was held constant during the course of the FTIR scan. The inset of Figure 13 depicts a steady increase in the methylene stretching vibrations as the temperature is ramped, confirming a reduction in the amount of crystallinity in the probed sample. At this point, we cannot comment on why there is no sharp transition between the liquid-like and semi-crystalline-like conformations of the chains.

3. Conclusion

We summarize by emphasizing several key points of the novel design of our surfaces. They represent the only known polymeric system we are aware of that responds almost instantaneously to wettability changes at room temperature ($\Delta\theta \approx 2^\circ \text{ s}^{-1}$ for PVMS-S-(CH₂)₂OH). This behavior results from the high flexibility of the siloxane backbone and the large disparity of surface energies between the hydrophobic methyl and the hydrophilic mercaptoalkanol side chains. The response rate depends on the number of methylene spacers in the mercaptoalkanol. While for $n = 2$ and 6, the surface reconstructs almost

instantaneously, $n = 11$ specimens resist reconstruction because of strong vander Waals forces leading to the formation of semi-crystalline regions. We have shown that liquid-like siloxane surfaces ($n = 2$ and 6) can be continually oscillated between polar and nonpolar states for at least ten cycles, with no loss of wettability for the 3-mercaptopropanol modified substrate. We confirmed the formation of semi-crystalline regions in PVMS-S-(CH₂)₁₁OH substrates through dynamic rheology, DSC, and FTIR-ATR. The analysis revealed a melting transition in PVMS-S-(CH₂)₁₁OH that was absent in PVMS-S-(CH₂)₂OH and PVMS-S-(CH₂)₆OH.

4. Experimental

PVMS Synthesis: Hydroxy-terminated PVMS was synthesized using the methodology described elsewhere [20]. Molecular weights and polydispersity indices (ranging between 4.9–78.7 and 1.5–3.0 kDa, respectively) were determined using size exclusion chromatography (SEC) with HPLC-grade toluene as a mobile phase. The SEC system was equipped with three Styragel 4.6 × 300 mm columns (models HR3, HR4, and HR4E, Waters Corporation, Milford, MA) for the polymer separation. The Optilab rEX (refractometer with EXTENDED range, Wyatt Technology, Santa Barbara, CA) was used as the concentration detector and a miniDAWN Tristar as the light scattering detector (Model WTR-02, Wyatt Technology, Santa Barbara, CA). With the intensity of light scattered and the absolute concentration measured, the molar mass is obtained. Polymer solutions with concentration of $\approx 2 \text{ mg mL}^{-1}$ were prepared. The solutions were filtered to SEC sampling vials with 0.2 μm PTFE syringe filters. The SEC data was processed with ASTRA software (version 5.1.9.1, Wyatt Technology, Santa Barbara, CA). The dn/dc of PVMS was determined by preparing exact solutions with concentrations ranging from 0–2.5 mg mL^{-1} of polymer in HPLC-grade toluene; two different batches of PVMS were selected for testing with the refractometer. The dn/dc value is represented by the slope of the DRI versus concentration, as shown in Figure S1 in the Supporting Information. As there appears to be a slight molecular weight dependence on the dn/dc value, samples were analyzed as deemed appropriate in ASTRA. An example PVMS run with changing molecular weights is shown in Figure S2 in the Supporting Information, where the final molecular weight of the polymer was determined to be $\sim 45 \text{ kDa}$ after 6 h at $\sim 110^\circ \text{C}$ (Table S1 of the Supporting Information). The kinetics of the reaction depends on the lithium hydroxide concentration and activity as well as the starting material (Dow Corning PJ Fluid) quality. Light scattering indicates a higher molecular weight peak in the final sample; this is a signature of an agglomerate/gel that occurs with long reaction times and does not contribute greatly to an overall higher molecular weight as the reaction rates slow down with time.

PVMS Network Formation: Chemical crosslinking of siloxanes can be accomplished with four types of common commercial reactions [40,41]: i) peroxide-induced free radical, ii) condensation reactions, iii) hydrosilylation addition reactions, and iv) hydridosilane/silanol reactions. In order to gain control over the cross-link densities and preserve the active vinyl group along the PVMS backbone, we utilize the condensation (or alkoxy-cure) reaction route that entails linking hydroxyl-terminated siloxanes with tetraethoxysilane (TEOS) in the presence of tin catalyst. This procedure results in a model tetrafunctional network, where the “liquid” nature of the siloxane backbone between junction points remains intact [42]. Our PVMS networks were formulated as previously described with the 36.3 kDa ($M_w/M_n = 2.25$) polymer [20]. In addition, PDMS networks were prepared by cross-linking monodisperse PDMS chains by following reported procedures [42,43] and by utilizing the commercial Sylgard-184 kit (Dow Corning). All other chemicals were obtained from Sigma-Aldrich Chemicals and used as received.

Thiol-ene Modification of PVMS Networks: The storage modulus (G') of elastomeric PVMS networks measured using the methods described below was found to be $\sim 8 \times 10^4 \text{ Pa}$ after Soxhlet extraction using toluene for at

least 48 h followed by drying at 75 °C under 30-mm Hg vacuum. The vinyl moieties on PVMS were subsequently saturated via azodiisobutyronitrile (AIBN)-initiated thiol-ene radical addition of HS(CH₂)_nOH (*n* = 2, 6, and 11)[44]. After the reaction, the samples (denoted as PVMS-S-(CH₂)_nOH) were re-extracted, dried, and stored in a low-humidity chamber. Experiments using IR spectroscopy confirmed that the grafting density of -S(CH₂)_nOH was approximately equal in each sample. In a typical thiol-ene addition reaction approximately 0.12 g of the extracted and dried PVMS network was placed at the bottom of a reaction flask. The sample was allowed to swell in 10 g of N₂-purged toluene overnight. A mixture of 1-dodecanethiol (0.22 g) and AIBN (0.0048 g) was purged with nitrogen and added to the reaction flask. The flask was capped and heated to 60 °C for 5–6 h. The PVMS-modified sample was removed from the flask then extracted in toluene for 48 h. After extraction the substrate was dried under 25 mm Hg vacuum at 70 °C for 1 day. The sample was stored in a desiccator until testing was performed. Substrates similarly modified with 3-mercaptopropionic acid were extracted in DI water, dried with nitrogen, and immediately tested for wettability.

Surface Reorientation: Organization of the thiol-based moieties on the PVMS surfaces were assessed via static contact angle (SCA) and dynamic contact angle (DCA) measurements using DI water (*R* > 15 MΩ cm). In a typical SCA experiment (sessile drop technique) experiments were performed with using a Ramé-Hart contact angle goniometer (model 100-00) equipped with a CCD camera, and analyzed with the Ramé-Hart Imaging 2001 software. The contact angles θ were recorded as a function of time (with 5 s increments for 5 min) after depositing 8 μ L of the probe liquid on the substrate (the error in $\theta = \pm 1.5^\circ$). The principle of DCA experiments is shown schematically in Figure S3 of the Supporting Information. Each cycle consisted of placing a nitrogen-purged rectangular (~10 × 10 × 1 mm³) PVMS slab above a beaker containing DI water at room temperature (Stage 1). The DCA stage was raised at a rate of 80 μ m s⁻¹ until the detection of the water-substrate interface (Stage 2). At that point, the stage was advanced for 3 mm, held for 8.5 min (Stage 3), and returned to its original position. The total water contact time was 9 min for each cycle. During each cycle, the DCA recorded the total force acting on the sample (*F_t*). *F_t* is related to contact angle through:

$$F_t = mg - V_s \rho_L g + P \gamma_L \cos(\theta) \quad (1)$$

where *mg* is the gravitational force zeroed out by taring the balance prior to the cycle run, *V_s* the volume of the solid immersed in water, ρ_L the DI water density, *P* the wetted sample perimeter, and γ_L is the surface tension of DI water. This technique facilitates measurement of advancing and receding contact angles as well as the change in contact angle during the sample hold-time. Since the immersed volume of the sample (*V_s*) remains constant during the hold-time, only the wetting force, $P \gamma_L \cos(\theta)$, changes as a function of time due to the surface reconstruction. After the completion of each cycle, the sample was blow-dried with nitrogen gas and another cycle was commenced. The lapse time between two consecutive cycles was ~7 min; ten wettability cycles were carried out for each sample.

Infrared Spectroscopy: FTIR-ATR was used to characterize chemical changes that took place on the modified PVMS surface. All spectra were collected using a BioRad/Digilab FTS-3000 FT-IR spectrometer using a mounted crystalline Ge, ATR sampling attachment (Pike Technologies inc., MIRacle Single Reflection ATR) with a normal spectral response of 650 to 5500 cm⁻¹. The infrared light was focused onto the photodiode of a liquid nitrogen-cooled, wide band mercury-cadmium-telluride (MCT) detector with a normal spectral response of 650 to 7000 cm⁻¹. There is nominally one reflection with a spot size of approximately 100 μ m. The spectrometer and attachment were purged with dry compressed air, which reduces the possibility of atmospheric water or CO₂ contamination of the spectra and samples. For each sample, 64 scans (10 repeats per sample) were collected using Ge-crystal detector with a resolution of 2 cm⁻¹ under constant nitrogen flux to eliminate the effect of water vapor on the collected data. The data were analyzed using BioRad-IR software. In addition the ATR element was fitted with a Peltier thermal heating and cooling chip allowing for temperature control of the samples ($\pm 70^\circ$ C above ambient). The

spectra presented are an average of 1 accumulation of 64 scans. Sample spectra were recorded over a temperature range from ambient to 50 $\pm 0.5^\circ$ C in 1–5 °C steps, with a resolution of 2 cm⁻¹. The spectra were converted into absorbance units by taking the negative of the log ratio of a sample spectrum to that of an air spectrum. The data were then transferred to data processing software (Microcal Origin, Microcal Software Inc., Northampton, MA), where numerical treatment and final graphs were prepared.

Differential Scanning Calorimetry: DSC was performed using a TA Instrument Q100. Two runs were carried out for each sample in the range of -80 to 130 °C with a heating rate of 3 °C min⁻¹ under a nitrogen atmosphere. The *T_g* values were determined as the onset points from the second scans if applicable. The melting point *T_m* was taken as the maximum of the endothermic peak.

Dynamic Rheology: Dynamic frequency sweeps were performed under isothermal conditions from 0.05 to 100 rad s⁻¹ on a Rheometrics Advanced Rheometric Expansion System (ARES) with a defined strain within the linear viscoelastic regime using a parallel plate geometry. Wall slip was minimized by applying a normal force for optimum plate contact producing repeatable results.

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