Effects of Functional Groups on Surface Pressure–Area Isotherms of Hydrophilic Silicone Polymers

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Organic/inorganic hybrid silicone polymers are increasingly used in cosmetics, inks and paints, and fabric care applications owing to their special Si–O bond characteristics. Because of the presence of organic as well as inorganic groups, they show the properties of both, and the presence of hydrophobic as well as hydrophilic character makes them behave like a hybrid polymer. Though they are widely used, the utilization of hydrophilically modified silicones on a large scale has mainly been empirical due to lack of fundamental knowledge about variation in their properties with systematic change in their structure. The choice of moieties for hydrophilic modification of silicones in most of the earlier works has been nonionic based on ethylene oxide and propylene oxide groups, however, very little is known about their ionic counterparts. The current work focuses on understanding the behavior of functionally grafted silicone polymers with respect to the variation in the hydrophilic part of the grafting chain. Hydrophilically grafted silicone polymers form monolayers at the air–water interface, which are stabilized by interactions of functional groups with water. The present work examined the effects of functional group modifications on the conformational behavior of chains at the interface. It was observed that the shape of the chain depends on the available area at the interface (or surface pressure), and there are conformational changes with an increase in the number of molecules per unit area. While a poly(dimethylsiloxanes) (PDMS) chain may undergo stretched to helix transition as predicted earlier, this may not be the case for hydrophilically grafted chains. On the basis of the shape of the surface pressure–area isotherm and correlation with the scaling theory, a gradation in hydrophilicity of functional groups and hence modified silicone chains at the air–water interface is predicted.

Introduction

Silicone surfactant is a generic name given to the molecules consisting of permethylated siloxane chain joined to one or more hydrophilic groups. The weak intermolecular attractive forces and special Si–O bond characteristics of silicone surfactants impart a unique dry-lubricity and bounciness to various substrates as compared to hydrocarbon surfactants. The choice of the hydrophilic moiety in most of the works in the past has been poly(ethylene oxide) to give a nonionic silicone surfactant.[1,2] A recent review in surfactant science series[3] describes the synthetic methods and surface active and phase behavior studies along with various applications such as de-emulsification in oil production, defoamers in fuels, and foam stabilizers in poly-urethane foams. Other work describes the utility of silicone surfactants in other industrial formulations such as inks, paints and coatings,[4] textiles, agriculture, and personal care products.[5] While much effort has been made to understand the nonionic silicone surfactants, very little is known about their ionic counterparts. Few preliminary works focused on cationic[6,7] and anionic[8] trisiloxane surfactants, and they found these trisiloxane surfactants to behave as excellent foaming agents.[9] Another work reported the synthesis and surface properties of zwitterionic silicone surfactant.[10] Although nonionic surfactants are very effective at lowering surface and interfacial tensions of aqueous as well as nonaqueous systems, they are unstable to pH variations and they hydrolyze to long-chain alcohols. Since long-chain alcohols are irritants, nonionic silicone surfactants are not very easy to be employed under all pH conditions. The objective of the current study is to understand the structure–activity relation-ship of functional polymeric silicone surfactants with respect to variation in the hydrophilic part of the grafted chain. Since most of the applications of modified silicones involve modification of interfacial properties, the present work focuses on the effect of functional groups on conformational behavior of the polymer at the air–water interface.

The surface pressure–area isotherm of poly(dimethylsiloxanes) (PDMS) has been investigated by many researchers in the past.[11–19] The initial work by Bank[11] and Ellison and Zisman[12]

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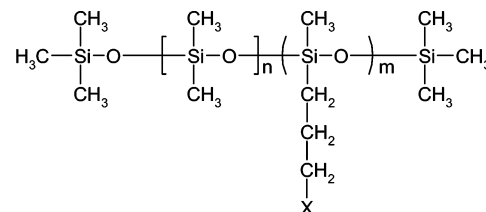
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focused on understanding the PDMS film on organic substrates. Newing[16] initiated work on modified siloxane showing the anchoring effect of the terminal OH group. It was shown by Jarvis[14] that polarity of subphase liquid is important for the stability and the insolubility of PDMS film. From a conformation point of view, several different structures have been proposed for conformation of linear PDMS chain at the interface. Damaschun[20] proposed a 6/1 helix with six backbone atoms per turn of the helix. On the basis of NMR spectra of crystalline PDMS, Flory[21] suggested a more extended conformation than Damaschun. An extended helical conformation was suggested on the basis of cis−trans arrangements in PDMS.[22] All of the three theories suggest helical conformations, but Bernett and Zisman[23] showed that trifluoro modification prevents formation of perfect helices because of steric hindrance of the bulky groups. A relatively recent work by Lenk et al.[19] has shown the effect of functional groups on the monolayer of the end-group modified PDMS at the air−water interface. They have also shown solubility of low molecular weight components in polydisperse systems.[24] While much work has been done on understanding air−water interface behavior of PDMS and end-functionalized siloxanes, very little is known about hydrophilically grafted silicone chains. The present work reports the effect of functional graftings on siloxane polymers at the air−water interface.

Experimental Section

Materials. PDMS was used as the reference compound in this study. PDMS of viscosity 50cSt was purchased from Sigma Chemical Co. and was used as received. Amino-modified polymeric silicone was synthesized from decamethyl cyclopentasiloxane (D5), tetramethylammonium hydroxide, and amino siloxane using equilibration process. The reactants were selected to have only one amino group per side chain. The ratio of reactants was selected to give an m:n ratio of approximately 1:7.5 (Figure 1), and the viscosity of the polymer was adjusted to 65 centipoise. The product was distilled to reduce the amount of D5 to less than 0.5%.
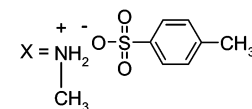
The cationic quaternary polymeric silicone surfactant was synthesized by methylation of the primary amino-modified polymeric siloxane (Figure 1). The quaternization reaction was carried out in bulk (without any solvents) using methyl tosylate as the quaternizing agent. The nature and bulkiness of the counterion does not significantly affect the surfactant film at the liquid−air interface because they are freely soluble in water. The stoichiometric ratio

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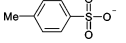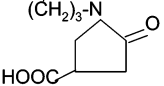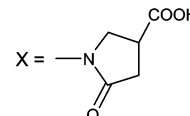

Figure 1. Structural representation of modified silicone polymer. The grafting ratio is denoted by m:n = 1:7.5.

was selected to obtain only 50% quaternization of amino groups as confirmed from amine value determination. Tosylate was added in a stepwise addition method, and the temperature of the exotherm was maintained below 50 °C by cold water jacketing to reduce the yellowing of the compound. The quaternized polymer was used as is without any further purification.

The reaction to synthesize the anionic polymeric silicone (Figure 1) has been carried out by reacting the amino-modified silicone polymer with itaconic acid as previously reported in U.S. Patents 5,596,061 and 5,807,955.[25] The reaction was carried out above 90 °C under controlled conditions for 3−4 h till the desired acid value was reached. Solvents were avoided to eliminate any contamination of the product. Here also, the stoichiometric ratio was adjusted to have only 50% acid modification and was confirmed from acid value and amine value analysis. The acid-modified polymer was used as is without any further purification.

All modifications were performed at Elkay Chemicals Pvt. Ltd., Pune, India. Anionic and cationic silicone surfactants were synthesized by modification of an amino-modified compound, and hence the polymers are expected to have the same chain length (and hence similar molecular weight and distribution). The structures and properties of the four compounds are listed in Table 1. The products were characterized by nuclear magnetic resonance (NMR) and infrared (IR) spectroscopic methods (data not shown). The absolute molecular weights of polymers are not known, but they are approximately 5000 on the basis of viscosity measurements.

Measurement of Langmuir Isotherms. A Nima Mini-Langmuir trough (model 601 M) with vibration isolation was used for surface pressure measurements. The trough and barriers are made of Teflon to avoid any contamination of the subphase. Wilhelmy plate method using a paper plate (20-mm perimeter) provided by Nima Technology was employed for surface pressure measurement. Langmuir isotherms were measured on Millipore water (18MΩ resistivity) subphase. Perfect wetting was ensured by first allowing the subphase solvent to completely wet the plate. The changes in surface pressure were measured using an electrobalance, which was connected to a computer. The resolution of the instrument is 0.1 mN/m. The surface of water was cleaned by using a micropipet aspirator. Chloroform, HPLC grade (with minimum purity of 99.9%) purchased from Pharmco Products Inc., was used as a spreading solvent. A solution containing 0.15 mg/mL concentration of a given polymer in the spreading solvent was fixed for all experiments after a series of experiments done at different solute concentrations. Twenty-five microliters of 0.15 mg/mL solution was spread on the water surface,

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Table 1. Structure and Properties of Hydrophilically Grafted Silicone Polymers

Compound	Structure	Viscosity (cps)	Amine value (mg KOH/gm)
Poly(dimethyl siloxane)	$Me_3SiO\text{-}[Me_2SiO]\text{-}SiMe_3$	50	-
Amino modified polymeric siloxane	$Me_3SiO\text{-}[Me_2SiO]_n\text{-}[MeSiO]_m\text{-}SiMe_3$ $(CH_2)_3NH_2$	65	83
50% quaternization of A with methyl tosylate	$Me_3SiO\text{-}[Me_2SiO]_n\text{-}[MeSiO]_m\text{-}SiMe_3$ $(CH_2)_3N^+H_2(CH_3)$	High (not analyzed)	35
50% modification of A with Itaconic acid	$Me_3SiO\text{-}[Me_2SiO]_n\text{-}[MeSiO]_m\text{-}SiMe_3$ $(CH_2)_3\text{-}N$	Very viscous, do not flow	48.8
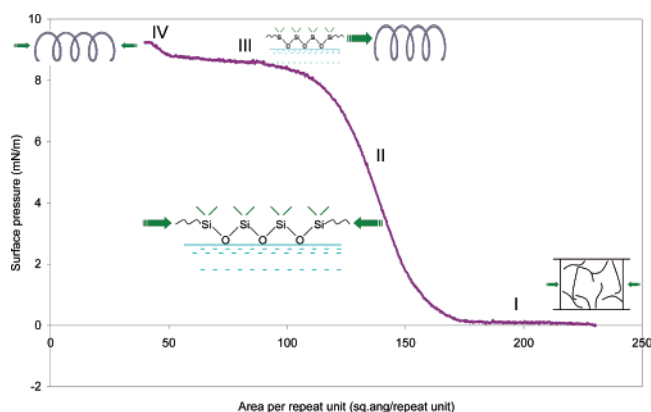
Figure 2. Surface pressure–area isotherms of poly(dimethylsiloxane) at air–water interface, pH of water = 6, ionic strength = 0.

Figure 3. Surface pressure–area isotherms of all compounds at air–water interface, pH of water = 6, ionic strength = 0. Black = PDMS, magenta = acid-modified silicone, blue = quaternized amino silicone, red = amino silicone.

and chloroform was allowed to evaporate for 20 min. The surface pressure measurements were initiated only after ensuring that pressure sensor was reading zero surface pressure. This also makes sure that the spreading solvent was free of any nonvolatile surface-active impurities. Constant temperature was maintained at 20 °C (±0.1 °C) using Neslab water bath recirculator. The compression rate of barriers was fixed at 5 cm²/min. All experiments reported here were done at pH 6.
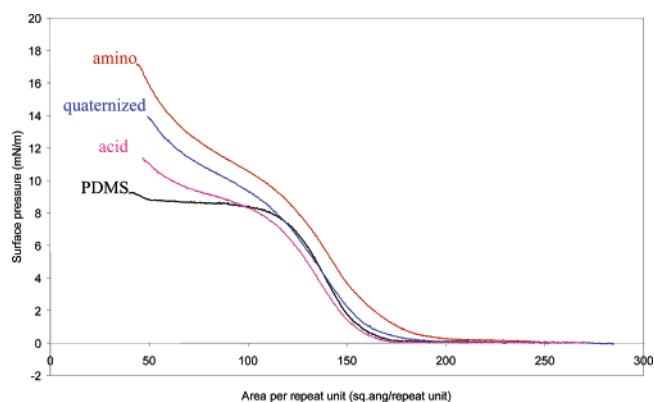
Results and Discussion

Conformation of Silicone Chain at Air–Water Interface. The surface pressure–area isotherm obtained for the reference compound PDMS is shown in Figure 2. The isotherm presents four regions. These data are in accordance with the PDMS isotherms of different molecular weights reported earlier.[19,26] From the isotherms and from other spectroscopic techniques, the following conformations are proposed for various regions.

Region I: The individual polymer chains are far apart and there is no chain–chain interaction in this region. The polymer lies in a fully stretched conformation where the oxygen atoms of the −O−Si(CH₃)₂− units are in contact with water, and methyl groups are pointing outward.

Region II: In this region, the polymer chains come close to each other and begin to touch. The rise in surface pressure indicates compactness of the polymer film.

Region III: The plateau in this region corresponds to gradual transformation or phase change of the monolayer. The individual

(26) Shapovalov, V. L. Langmuir monolayers of polydimethylsiloxane with controllable surface potential. *Thin Solid Films* **1998**, *327−329*, 816−820.

stretched chains have no further means to compress, and hence they are forced to change their conformation to a new one occupying a smaller surface area. The plateau represents transition of stretched chain to helices.

Region IV: Slight increase in surface pressure reflects the formation of densely packed layer of helices. Once dense packing is achieved, there is no further place for helices to compress. Hence, rather than deforming the stable helical conformation, the chains prefer to slide over one another giving rise to another plateau region.

All amino-, quaternary-, and acid-modified compounds have one hydrophilic grafting chain per approximately 7.5 dimethylsiloxane units. Hence, to have comparable repeat units, one repeat unit of PDMS includes about 8.5 dimethylsiloxane units. The area per repeat units observed in Figure 2 is accordingly adjusted.

The isotherm of amino-modified silicone chain is similar to PDMS isotherm in region I and region II (Figure 3). However, in region III, instead of plateau, further increase in surface pressure is observed in the case of amino-modified silicone polymers. Similar regions I and II indicate that the amino-modified siloxane, like PDMS, is fully stretched in regions I and II and the chains compress without any conformational change. In the case of region III in PDMS, there is a change in conformation from straight chain to helix, which necessitates pulling some of the oxygen atoms out of the water subphase. It is relatively easy to pull oxygen atoms out of water and to form the helix since there is no strong interaction between the PDMS chain and the water
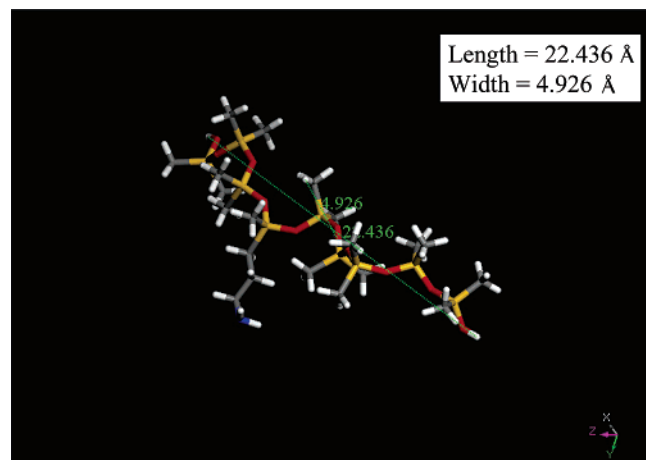
Figure 4. Molecular modeling of amino-modified silicone repeat unit in a vacuum to calculate the parking area on air−water interface. Repeat unit length = 8 dimethylsiloxane and 1 grafting chain.

Figure 5. Surface pressure−area isotherms of different percentage acid modified silicone polymers at air-water interface, pH of water = 6, ionic strength = 0.

subphase. In the case of amino-modified siloxane, the amino grafts stabilize the polymer chain on the surface of water and hence act as tying points or anchors for the chains to water. To form helices of amino siloxane in region III, it is required to pull some of these anchors out of water. Since it would be relatively difficult to pull out amino groups from water, the amino chains further compress, and this leads to an increase in surface pressure. The slope of the line in region III is decided by the competitiveness of two simultaneous phenomena: compression of amino silicone chains and pulling out amino anchors from water.

The grafting chains of functionalized polymers are immersed in the water subphase, and hence the length of backbone chain determines the parking area of a repeat unit. The repeat unit of amino-modified silicone polymer chain consists of 1 unit of m per approximately 7.5 n units (Figure 1). Therefore, the backbone length that characterizes a repeat unit is 8.5 times the length of a Si−O bond. On the basis of van der Waals radius and bond lengths of Si−O, Si−C, and C−H bonds, the parking area of a fully stretched chain is approximately 136 $Å^2$. Molecular modeling was also performed for amino-modified silicone polymer as shown in Figure 4, which suggests that the repeat unit area is about 110 $Å^2$. Observed surface pressure isotherms show transition from region II to region III near about 120 $Å^2$/repeat unit. When in the case of molecular modeling, curling of amino-modified silicone polymer in a vacuum underestimates the length of stretched siloxane chain at the air−water interface, the bond length calculation depicts ideally stretched behavior and hence overestimates the repeat unit chain length. Hence, bond length calculations and molecular modeling are coherent with the observation that the chains can be in stretched conformation in region II but have to reconform when they enter into region III. In the case of PDMS, it has been established that chains undergo stretched−helix transition from region II to region III. Work done by Lenk et al.[19] have shown that the chains of end-functionalized siloxane also undergo stretched−helix transition from region II to region III. The modified silicone polymers have the grafted chains of random copolymers with atactic configurations. Moreover, silicone backbone is very flexible in nature, and hence it can easily orient itself in such a way that the hydrophilic functional groups can be immersed in water. It can be assumed that all the functional groups of a particular polymer are immersed in water and need to be pulled out to form a helix. It is not clear in this case whether the grafted silicone chains form simple loops or helices in region III. Also, because of the difficulty in pulling the functional groups out of
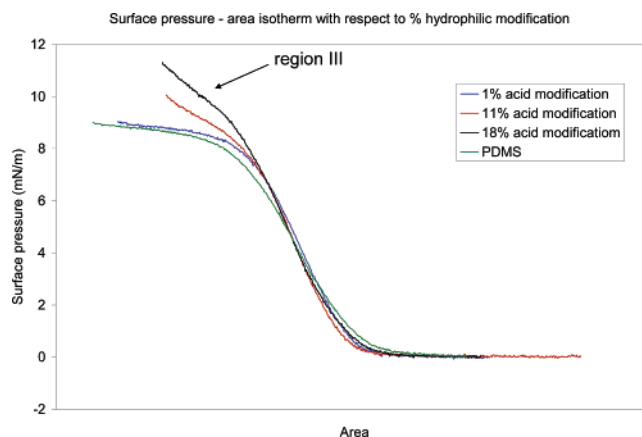
the water, the functionalized silicones do not undergo ideal phase transition (showing constant surface pressure) as seen in the case of PDMS.

Effects of Functional Groups. When the isotherms of different functional graft modifications (Figure 3) are plotted on the same graph, all the curves look almost the same down to about 120 $Å^2$/repeat unit (i.e., in regions I and II), with slight differences possibly because of minor variations in the equivalent weights of respective polymers. This is proposed to be due to the stretched conformation of chains in regions I and II, where only chain lengths play a governing role and not the functional groups. On further compression, between 120 $Å^2$/repeat unit and 50 $Å^2$/repeat unit, the chain undergoes a transition from stretched conformation to helical or loops. In this process, some of the functional groups are pulled out of water. The functional group that interacts most strongly with water will offer maximum resistance to come out of water. Hence, the chain having more affinity for water undergoes higher compression and shows higher surface pressure. On the basis of this hypothesis, the slope of the curves in region III can be considered to be a measure of the hydrophilicity of the functional groups on the chain. To further confirm this hypothesis, surface pressure−area isotherms were measured with different % hydrophilic modification (Figure 5). It was observed that with increase in % modification, the slope of region III increased, illustrating that the slope of region III depicts the degree of hydrophilicity in various silicone chains. Also, it can be seen that in the case of 1% modification (one functional group per polymer chain), we can still see the phase transition as in the case of PDMS, but in the case of 11% modification the ideal phase transition is not observed. Because of different % hydrophilic modifications, different isotherms in Figure 5 fall at different area per repeat unit regions. Here, all the curves are arranged to superimpose regions I and II to see the trend in region III.

According to this theory, Figure 3 shows that the increasing gradation of affinity of functional groups for water is amino > quaternary amino > acid modified > unmodified. Similar trends have been reported in the past for end-functionalized silicone chains.[19] The same trend was observed under all pH conditions.

Use of the Scaling Theory. When an amorphous polymer is spread on a liquid support to form a monolayer, a surface pressure exists that is analogous to the osmotic pressure characteristic of three-dimensional solutions.[27] The present approach makes use

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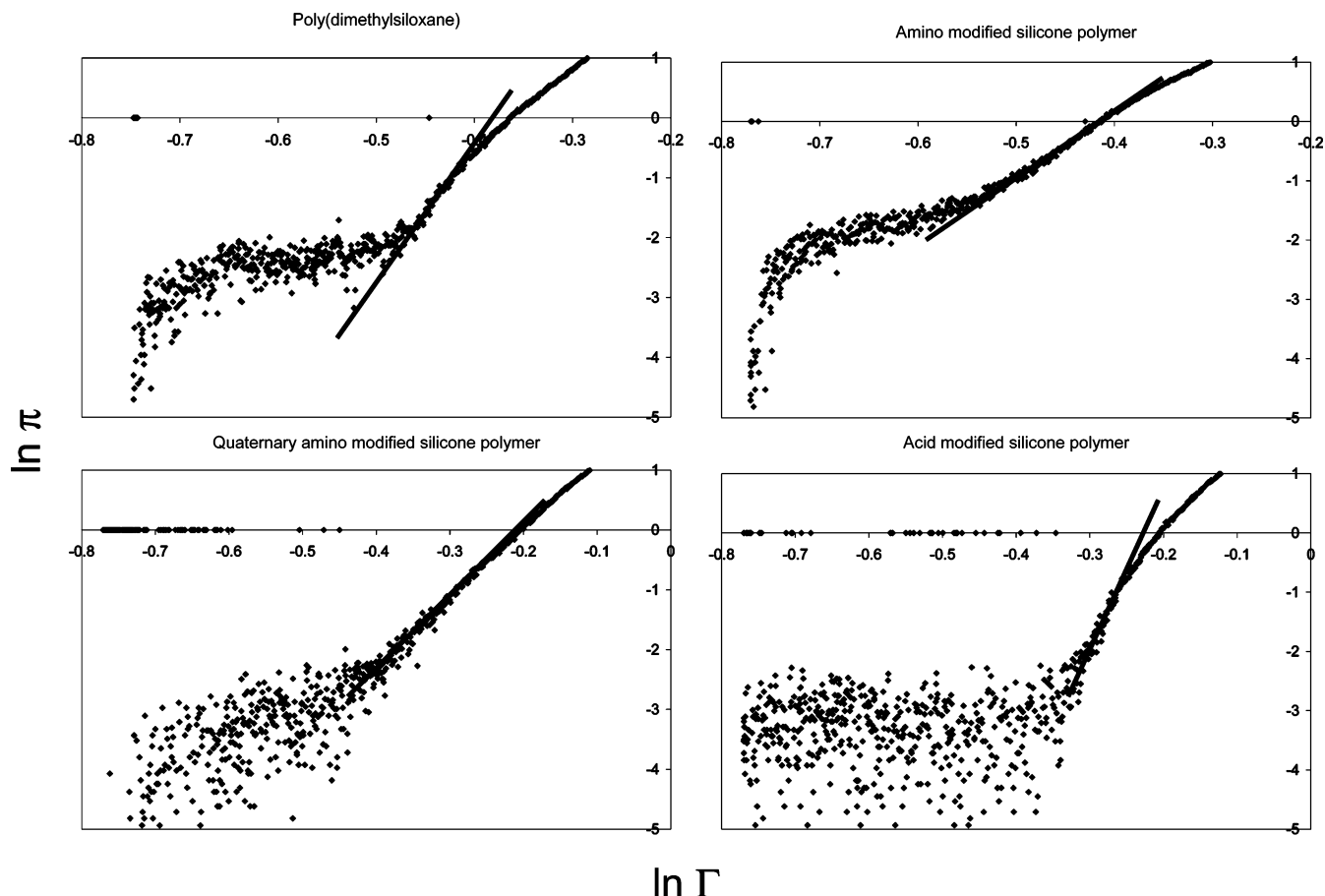
Figure 6. Plot of ln π vs ln Γ in the semidilute region of the surface pressure−area isotherm to obtain the characteristic critical exponent of excluded volume.

of the scaling theory[28] to establish connection between the functional group and stability at the air−water interface by making use of the relationship between surface pressure and concentration. Similar works have been done in the past,[17,18,29−32] but their work focuses mainly on finding the second virial coefficient value. Leiva et al.[31] correlated the second virial coefficient with the good or theta solvent nature of air−water interface for poly-(itaconates), but their aim was not to correlate with the modifying functional groups.

According to the scaling theory, in semidilute concentration region, surface pressure (π) obeys a power law relationship with surface concentration (Γ) and is independent of molecular weight. Hence, in semidilute regime, where the polymer chains partially penetrate the region of influence of other chains, the relation between π and Γ can be given by eq 1:

$$\pi = \Gamma^{d\nu/(d\nu - 1)} \qquad (1)$$

where d is dimensionality and ν is characteristic critical exponent. Theoretical predictions for chains in two dimensions are that ν

is equal to three-fourths, four-sevenths, and one-half for good solvent,[29] theta solvent,[33] and poor solvent[34] conditions, respectively.

In region I of the surface pressure−area isotherm, the chains are believed to be far apart and to not interact with each other. Each chain lies separately on the water surface and interacts with just the water subphase. In region II, the chains start touching each other and they influence the neighboring chains. The onset of region II can be correlated with the semidilute region, and hence eq 1 mentioned above can be utilized to analyze the isotherms and to obtain a quantitative insight. The area per repeat unit in the Langmuir isotherms was converted to surface concentrations, and eq 1 was used to plot ln π versus ln Γ in the semidilute regime and to obtain the characteristic critical exponent for the given system. The plot is shown in Figure 6.

According to eq 1, the plot of ln π versus ln Γ in the semidilute region should show a linear variation with slope of $2\nu/(2\nu - 1)$. Figure 6 shows this double logarithmic plot, and the values of ν calculated from the slopes of each curve are represented in Table 2. Though there is some dispersion of points in the figure at low surface concentrations, as also seen in other works,[31] there is a clear distinction between the slopes of the curves. The observed critical exponent values support the hypothesis that stability of various silicone chains in two-dimensions is governed by their functional groups. It can be observed from Table 2 that amino and quaternary amino-modified silicone chains have a

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Table 2. Second Virial Coefficients and Characteristic Critical Exponent Values as Obtained from Scaling Concepts

compound	critical exponent
amino-modified polymeric siloxane	0.553
50% quaternization of A with methyl tosylate	0.544
poly(dimethyl siloxane)	0.525
50% modification of A with itaconic acid	0.524

value of close to 0.55, which indicates proximity to theta solvent conditions ($\nu = 0.571$) as opposed to PDMS and acid-modified silicone chains where the values are closer to poor solvent conditions ($\nu = 0.5$). This observation further confirms that in semidilute conditions amino and quaternary amino-modified chains are relatively more stable at the air−water interface than PDMS and acid-modified chains. The absolute values of critical exponents confirm the gradation in hydrophilicity of the functional groups studied in the present work. The critical exponent shows that the air−water interface resembles close to poor solvent conditions for acid-modified silicone polymer (even for the highest % acid modification).

Conclusions

Hydrophilically grafted silicone polymers form monolayers at the air−water interface, which is stabilized by interaction of functional groups that are submerged in the water subphase. Silicone chains assume a fully stretched conformation in regions I and II. The isotherm behavior in this region is guided mainly by the chain length and hence is independent of the nature of modification. As the surface is compressed, the chains are forced to change their conformation. In the case of PDMS, stretched to helix conformation change is relatively easy and hence a plateau is observed in the isotherm. For functional silicones, the formation of helix is resisted by the interaction of functional groups with water, and hence there is a simultaneous conformational change and compaction of the chains. This leads to differential slopes of isotherms in region III, depending on the predominance of one of the two mechanisms. The higher the affinity of functional group for water, the steeper the surface pressure curve in region III is. The characteristic critical exponents of excluded volume were obtained by application of scaling concepts in semidilute region of the isotherms. The values of critical exponents further corroborate the gradation in the hydrophilicity of functional groups obtained from region III of the isotherms. They also show that while all the chains are in theta solvent conditions at the air−water interface, amino and quaternary amino-modified silicone chains are relatively more stable than the acid-modified and PDMS chains. The detachment of functional groups from liquid phase decides how easily the polymer chain can be removed from the interface, which would impact the stability of the liquid−air interface. This is very important for widespread application of silicone surfactants in foam stabilization.

Note Added after ASAP Publication. This article was released ASAP on October 7, 2006. Figure captions 5 and 6 have been revised. The correct version was posted on October 12, 2006.