

Effect of Modifying Functional Groups on Interfacial Behaviour of Hybrid Silicone Polymers

Somil Mehta,¹ P. Somasundran,¹ Omprakash Yemul,² Ravi Kulkarni^{2*}

¹NSF Industry and University Cooperative Research Center for Advanced Studies in Novel Surfactants, Columbia University, 500W 120th street #911 New York, NY 10027

²Research and Development Department Elkay Chemicals Pvt Ltd, J 152/153 MIDC Bhosari Pune - 411026, India.

Abstract:

Modified silicones behave both as hydrophobic and hydrophilic polymers. Though widely used, their utilization has mainly been empirical due to lack of fundamental structure-property relationship. Most earlier works employ nonionic (ethylene oxide and propylene oxide) moieties for modification, however very little is known about their ionic counterparts. The current work focuses on understanding the conformational behavior of functionally grafted silicone polymers with variation in the hydrophilic grafting chains. It was observed that conformation of the chain depends on available area at interface, and the required transition energy depends on the extent of interaction of functional grafting with water.

Key Words:

Hydrophilically modified silicones, air-water interface, Langmuir isotherm, hydrogen bonding

Introduction:

Polysiloxanes are useful polymers because of their high chemo-, thermo- stability and nontoxicity. The desired properties can be achieved by attaching suitable modifying group to the silicones. Such organic/inorganic hybrid silicone polymers are increasingly used in cosmetics; inks, paints, and fabric care applications. Though widely used, the utilization of modified silicones has largely been empirical due to lack of fundamental knowledge. In most of the earlier studies the hydrophilic modification of silicones are based on non-ionic moieties[1,2]. There is little information available about their ionic counterparts. The present work is focused on the effects of functionality on the conformation of chains at the air-water interface.

Materials:

Poly(dimethyl siloxane) (PDMS) was used as the reference compound in this study. PDMS of viscosity 50cSt purchased from Sigma Chemical Co. was used as received. Amino modified silicone (AMS) was synthesized from decamethylcyclopentasiloxane (D5), tetramethyl ammonium hydroxide, and mono amino siloxane by equilibration process. The ratio of the reactants was selected to give m:n ratio of approximately 1:7.5 (figure 1) and the viscosity of the polymer was adjusted to 65cps. The cationic quaternary polymeric silicone (QAS) surfactant was synthesized by methylation of the primary amino modified polymeric siloxane, where as synthesis of the anionic polymeric silicone (IAS) was carried out by reacting the amino modified silicone polymer with itaconic acid[3]. All modifications were performed at Elkay Chemicals Pvt. Ltd., Pune, India. The detailed synthesis procedure is described elsewhere[4].

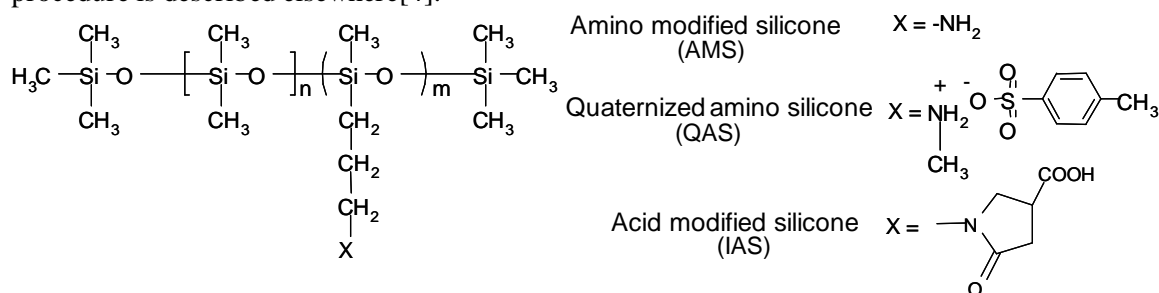


Figure 1: Structural representation of modified silicone polymers. (m:n ~ 1:7.5)

Results and Discussion:

Conformation of silicone chains at air-water interface:

The surface pressure – area isotherm obtained for the reference compound PDMS is shown in figure 2. The isotherm shows four regions[5], which suggest the following conformations in various regions:

Region I: The individual polymer chains are far apart and 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 pointing outwards.

- Region II: In this region, the polymer chains come close to each other and begin to touch. The rise in surface pressure indicates compacting of the polymer film.
- Region III: The individual stretched chains have no further place to compress, and hence they are forced to change their conformation to a new one occupying a smaller surface area. The plateau in this region indicates a gradual conformation transition
- Region IV: The slight increase in the surface pressure indicates further compaction of the chains.
- The hypothesis of change in conformation between region II and region III was also tested by van der waals bond length calculations and computer simulation.

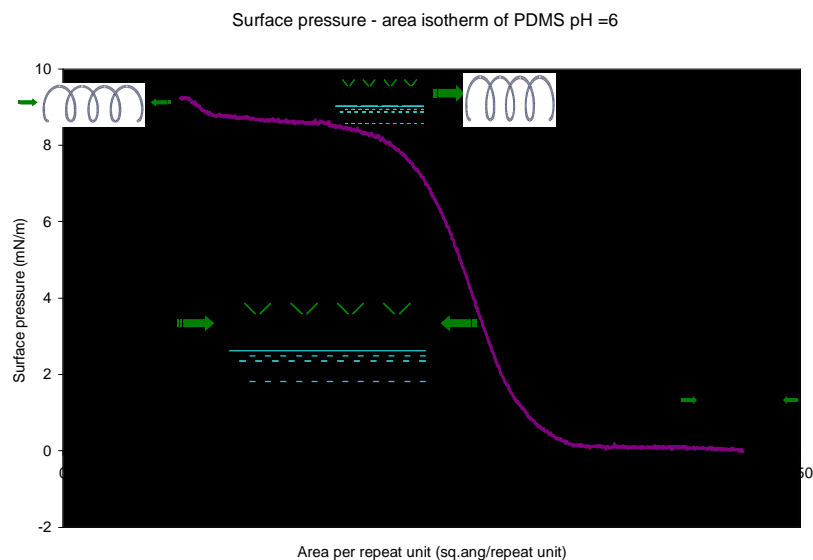


Figure 2: Surface pressure – area isotherms of poly(dimethylsiloxane) (PDMS) at air-water interface, pH of water = 6, no ionic strength. A repeat unit of PDMS constitute 8.5 dimethyl siloxane units in order to be comparable with modified silicones.

The isotherms of modified silicones are similar to PDMS isotherm in regions I and II (figure 2). Slight differences may exist in the isotherms because of slight difference in the equivalent repeat unit weight. Similarity of regions I and II indicate that the modified siloxane, like PDMS, are fully stretched in regions I and II. In region III, instead of plateau further increase in surface pressure is observed for modified silicone polymers. While a straight chain to helical transition is predicted for PDMS, the same hypothesis can not be extrapolated for modified polymers. This is because the functional grafts stabilize the modified chains on the water surface and thus act as tying points or anchors. To form helices, it will be required to pull many functional groups out of water, which is not as easy as in the case of PDMS. The modified chains continue to compresses in region III leading to 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.

Calculation of energy required in conformation transition

The increase in surface pressure during stretched to coil transition can be correlated with the energy required to bring about the conformation change. Hence the energy changes involved in changing the conformation can be calculated as demonstrated follows for PDMS.

The change in surface area and increase in surface pressure during region III can be found by linear approximation of the isotherm regions.

$$\text{Area change in region III} = 110 - 50 = 60 \text{ sq.ang/repeat unit}$$

$$\text{Therefore, number of repeat units per cm}^2 = 1/(60 \times 10^{-16}) = 1.667 \times 10^{14} \text{ repeat units/cm}^2$$

$$\text{Surface pressure change} = 0.5 \text{ mN/m} = 0.5 \text{ ergs/cm}^2$$

$$\text{Therefore, energy change} = (0.5 \times 6.023 \times 10^{23}) / 1.667 \times 10^{14}$$

$$= 1.8069 \times 10^9 \text{ ergs/mole of repeat unit}$$

$$= 43.021 \text{ cal/mole of repeat unit}$$

$$1 \text{ kT} = 4.0434 \times 10^{-21} \text{ J (at } 20^\circ\text{C)} = 579.84 \text{ cal/mole}$$

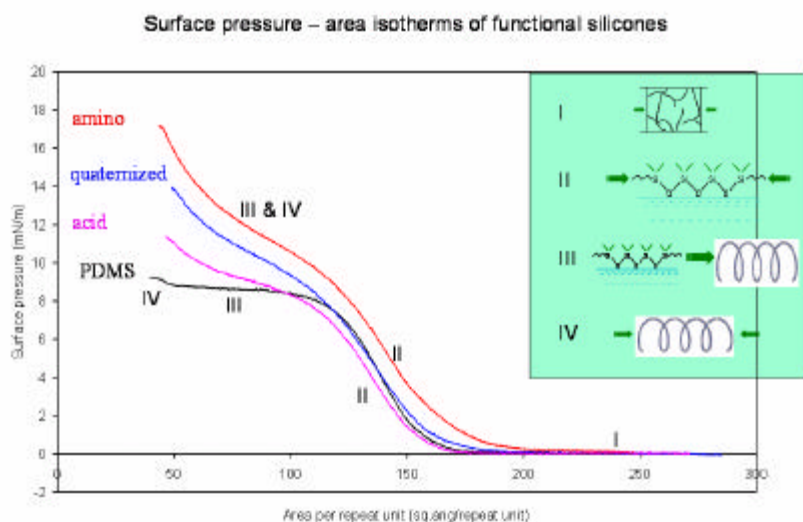


Figure 3: Surface pressure – area isotherms of all compounds at air-water interface, pH of water = 6, no ionic strength. Black = PDMS, Magenta = Acid modified silicone, Blue = Quaternized amino silicone, Red = Amino silicone.

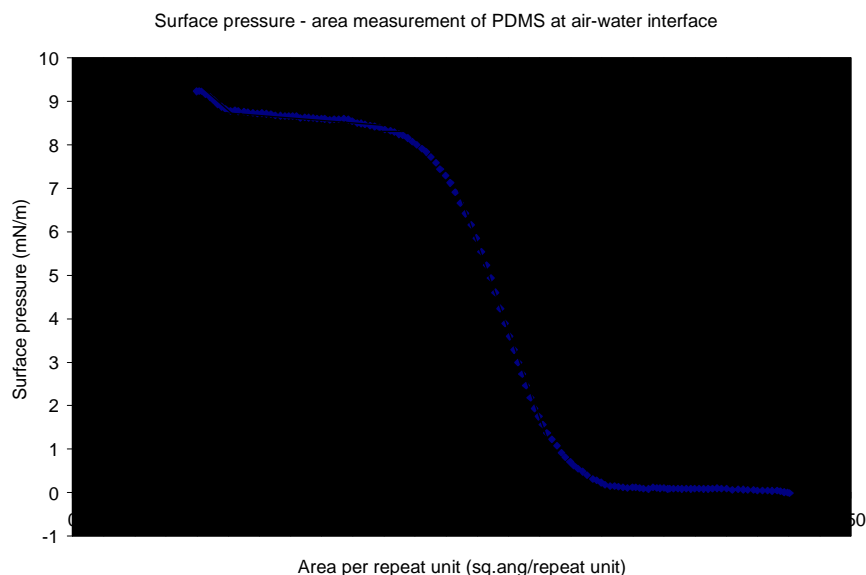


Figure 4: Surface pressure – area isotherms of all compounds at air-water interface, pH of water = 6, no ionic strength. Black = PDMS, Magenta = Acid modified silicone, Blue = Quaternized amino silicone, Red = Amino silicone.

Hence energy change in conformation transition of a mole of PDMS repeat unit $\sim 7.42\%$ kT . Each repeat unit of PDMS (here) involves about 8.5 -Si-O- bonds (dimethylsiloxane units). Hence it can be assumed that about 8.5 oxygen atoms are in contact with water in region I and II. Out of them let's say 7.5 come out of water to form helix. Hence each O-H₂O contact has energy equivalent to about 1% of kT . This value is very small compared to the energy of hydrogen bonds in water, which is $\sim 1kT$. Hence the energy changes involved in conformation change of PDMS are really small.

Similar calculations for other polymers were done and the result is summarized as follows:

Compound	Area change (sq. ang/repeat unit)	Energy change		
		(erds/sq.cm)	(cal/mole repeat unit)	kT
PDMS	60	0.5	43.021	0.0742
AMS	60	5	430.21	0.742
QAS	50	3.4	243.79	0.4204
IAS	50	2	143.4	0.247

The functionalized silicones have only one functional group per repeat unit. Hence, for example, the amount of energy required to pull an amino group out of water in AMS chain at air-water interface is approximately 0.75kT (assuming that all the amino groups are pulled out of water during transition). Similarly energy required to pull an acid group out of water requires about 0.25kT and a quaternary amino group requires about 0.4kT.

Conclusions:

Silicone chains were observed to 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 further compressed, the chains are forced to change their conformation, which constitute region III. In the case of PDMS, a plateau in region III may indicate stretched to helix transition, whereas this helix formation in functional silicones is resisted by the interaction of functional groups with water, and hence leading to simultaneous conformational change and compaction of the chains. Compaction leads to differential slopes of region III for different modifications, which in a way indicate affinity of the functional group with water. The energy required for pulling the functional groups out of water was computed from the increase in surface pressure in region III, and was observed to be in the range of 0.25kT to 0.75kT. 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.

References:

[1]. R. M. Hill, *Silicone surfactants; Surfactant science series*. Marcel Dekker: New York, 86, 1996.

[2]. E. D. Goddard, K. P. Ananthapadmanabhan and P. Chandar, *Langmuir*, 11, 1995, 1415.

[3]. A. Berger, D. L. Fost, U.S. Patent 5,596,061, 1997; U.S. Patent 5,807,955, 1998.

[4]. S. C. Mehta, P. Somasundaran, C. Maldarelli and R. Kulkarni, *Langmuir*, 22(23), 2006, 9566.

[5]. T. J. Lenk, D. H. T. Lee and J. T. Koberstein, *Langmuir*, 10(6), 1994, 1857.