Investigating the Conformation of Polymeric Dispersant Molecules on Nanoparticle Surface

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Summary: Block copolymers are widely used as stabilizers in industrial dispersions. These polymers adsorb on surfaces by an anchor chain and extend by a hydrophilic chain. Scaling model or de Gennes theory has been used to determine the grafting density of the block copolymers. By implementing this theory to the block copolymers, conformation of the polymer molecules as a function of distance between adjacent anchor chains can be determined.

The scaling model was applied to a selection of block copolymers (PE/F 103, PE/F 108, NPE1800, Triton X100, Triton X405, Lugalvan BNO12, Hypermer LP1, Hypermer B246 and OLOA 11000) in this study. The cross sectional area σ_c, distance s (square root of σ_c) and the Flory radius (end to end dimension of polymer), R_f, for all the polymers was determined. The cross sectional area per PEO (Poly Ethylene Oxide) chain (nm^2) was found to be increasing with the size of stabilizing chain. Triton X100 and Lugalvan BNO12 has the smaller stabilizing chains so occupy smaller cross sectional areas whereas PE/F108 and triton X405 have larger number of PEO units and occupy a larger cross sectional area. This shows that stabilizing chain regulates the adsorption amounts that are lower in case of lower number of EO units.

The application of de Gennes theory to experimental results suggested brush configuration of adsorbed polymer molecules in case of PE/F 103, PE/F 108, Triton X100, Triton X405, NPE1800, Lugalvan BNO12, Hypermer B246 and OLOA 11000. Whereas, Hypermer LP1 is more likely found to be adsorbed on graphitic carbon black in loops and trains.

Keywords: Flory Radius, Polymeric Dispersions, De Gennes Theory, Grafting Density, Blobs Theory.

Introduction

Considerable research has been reported on stabilization of various adsorbents in aqueous and non aqueous medium by using surfactants and/or polymers due to the diverse industrial applications of nano scale solid liquid dispersions [1-6]. Carbon nanotubes are widely utilized as fillers due to their extraordinary characteristics. Carbon nanotubes set themselves into aggregates so keeping them dispersed is of keen interest. Since the Carbon nanotubes are toxic and carcinogenic, therefore, graphitic carbon black having similar structure and properties has been selected as a model for the nanotubes.

Structured polymers/non-ionic dispersants (such as block copolymers) are frequently used for steric stabilization of nanoparticle dispersions. The structure of non-ionic dispersants is somewhat similar to the ionic dispersant as far as the hydrophobic part is concerned, while the hydrophilic part is generally made of polyethylene oxide chains. In practice, homopolymers cannot provide sufficient steric forces because they provide strong adsorption to the surface and good solvency in water as well. However, non-ionic block copolymers do this job well and prove to be very effective. An effective block copolymer dispersant must have an anchor chain with a strong affinity for adsorption onto the surface and poor solvency in a medium while the hydrophilic chains must extend far into the solvent to provide a sufficient steric barrier. Various conformations are adopted by dispersants onto the interface and this depends upon the structure of dispersant.

Fig. 1 presents the conformations of polymer molecules on the interface based on their structures. In case of a homopolymer, whole polymer may adopt a flat conformation if all the segments of the dispersant have high affinity to the interface, Fig. 1 (a). An example of this homopolymer is Hypermer LP1 (homopolymer of polyhydroxystearic acid) which was used in this study. While the block and graft copolymers have the most favourable structures. The AB block polymers have one B chain for strong adsorption and an A chain for good solvency in the medium, Fig. 1 (b), ABA block copolymers have two stabilising chains, Fig. 1 (c) [7]. Effect of the stabilizing chain molecular weight and the nature of anchoring group of polymers onto the stability and adsorption affinity are well reported. Sluzarenko *et al*. [8] used three di-block copolymers of polystyrene-b-polyisoprene, two high molecular weights and one low molecular weight for preparing

multiwall carbon nanotubes dispersions in dimethyl formamide (DMF), a polar solvent, and heptane, a non polar solvent. They found that both high molecular weight block copolymers show better stabilizing effect as compared to the low molecular weight block copolymer. They suggested that the low molecular weight polymer did not provide a sufficiently large repulsive barrier. Shoji and Shigenori [9] used ethoxylated polymers which have one hydrophobic part adsorbing onto the particles and other hydrophilic part which extends into the medium stabilizing the particles in water through the steric effect. They studied the effect of chemical structure of dispersants and concluded that the hydrophilic part should have sufficient length to negate the van der Waals forces. Abe and Kuno [10], Corkill *et al.* [11] and Ottewill [12] suggested that the adsorption of polyethylene oxide-polypropylene oxide-polyethylene oxide ABA copolymers (PE/F 103 and PE/F 108) which have the same size anchoring group but different ethylene oxide (EO) chain weights, is larger in molar terms for the polymer with low molecular weight EO chain, and suggested that the higher molecular weight EO chain crowded the surface and prevent further adsorption. Kronberg [13] found that the adsorption affinity of nonylphenyl ethoxylate depend on the size of EO units (number of ethylene oxide units) and it decreases with the increase of EO units. Later Kronberg [14] reported the adsorption of nonylphenyl polypropylene oxide-polyethylene oxide NPE type surfactants and pointed out that the adsorption of these kinds of surfactants depends upon the structure of the surfactant rather than adsorbing surface. Boomgaart *et al.* [15] and Pingret *et al.* [16] reported that the adsorption amounts in weight of NPE surfactants (NPE1800, NPE A, NPE B and NPE C) was constant for both hydrophobic silica and polystyrene latex and they scaled the anchoring distance s (square root of cross sectional area of polymer molecule) with the adsorbed layer thickness. They considered that the maximum adsorbed amount is governed by size of the EO segments rather than by hydrophobic portion. In non aqueous media, the stability of suspensions requires a polymer with an oil soluble stabilizing chain and a head group with strong adsorption affinity onto the adsorbing surface. The examples of these polymers are Hypermer B246 (an ABA block copolymer with an A (polyhydroxystearic acid) as stabilizing chain and B (polyethylene oxide) as an anchoring group and OLOA 11000 which is an AB copolymer with A (polyamine polar head group) and B (polyisobutylene) as a stabilizing chain (used in this study). Tomlinson *et al.* [17] constructed the adsorption isotherms of succinimide dispersants with different chain lengths and found the optimum chain

length (acting as a lipophilic part) which gives higher adsorption and hence the better coverage of the surface which is a requirement of a stable dispersion. Kim [18] demonstrated the effect of chemical structure of dispersant on the dispersal properties of nanotubes in organic media. He reported that the hydrophobic group must be strongly anchored to the hydrophobic CNT surface and the stabilizing species called the tail groups should be sufficient to provide steric hindrance. In his study he used hexylthiophene because thiophene group can be easily adsorbed onto the CNT surface as it has strong electro negativity while the hexyl group can provide steric hindrance in organic solvents. Gupta and Bhagwat [19] observed higher adsorption amounts for surfactants with benzene ring in their structures, for example, they found higher adsorption in the presence of SDBS than SDS for graphitic carbon black. So the structure of the hydrophobic group is also important in terms of adsorption and by consequence in the stability of suspensions.
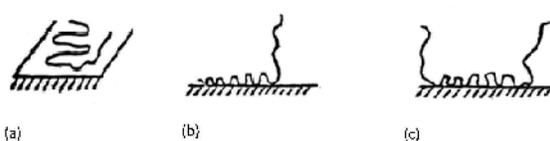

Fig. 1:   The conformations adopted by polymeric surfactants adsorbed onto the solid surface: (a) polymeric chain lying flat on the solid surface; (b) AB block copolymer with loop of B block and train configuration of long tail of A; (c) ABA block copolymer with two A's [7].

Dubois-Clochard *et al.* [20], found that increase of amino groups in polar anchoring part of succinimide dispersant increase the adsorption affinity of dispersant onto the adsorbing surface which plays an important role in the stability of the suspensions. Shen and Duhamel [21] investigated the role of secondary amines in polar anchoring core of succinimide dispersant in the enhancement of the adsorption affinity and the better coverage of the surface.

Hence one may conclude that the thickness of the steric barrier and the adsorption affinity of polymers can be altered by varying the stabilizing chain and anchoring chain. In this study, the effect of molecular structure on the conformation of polymer molecule adsorbed onto the carbon black particles is investigated.

In the literature, different theories have been reported for the description of the adsorption of polymers onto the surface. The Fleer and Scheutjens [22] theory is a lattice based theory with assumption

that each site of lattice is covered by a polymer segment. The configuration can be drawn from the surface and solvent mixing Flory-Huggins parameters and hence polymer segment density profile can be calculated.

The scaling theory or De Gennes theory [23] is another approach for the description of adsorption of polymeric dispersants in good solvents with a small energy of adsorption onto the surface. The density of the polymer segments in the adsorbed layer is determined as a function of distance from the surface and consequently the adsorbed layer thickness is calculated. In scaling theory the space around the surface is divided into three regions:

(a) The surface adjacent region of very short thickness and where the density of polymer segment depends upon the adsorption energy.
(b) The central region where the density of polymer segments is lower than the surface proximal region but higher than the density in bulk solution and is governed by the mutual interactions of polymer chains.
(c) The distal region in which density of polymer segments drops fast to the bulk concentration. By implementing this theory to the block copolymers used in this study, the conformation of the polymer molecule as a function of distance between anchor chains, s, also called the grafting density can be determined.

The separation distance "s" between each terminally grafted polymer chain is calculated as the square root of the area of polymer molecule "σ_c" calculated from the following

$$\sigma_c = (\Gamma_m N_A)^{-1} \qquad (1)$$

where Γ_m is the maximum amount adsorbed and N_A is the Avogadro number.

The flory radius, R_f, which is end to end dimension of polymer molecule is calculated from the Flory Huggins theory as given in equation 2 [23-24]:

$$R_f = a N^{3/5} \qquad (2)$$

where "a" is the size of monomer unit and "N" is the number of monomer units.

If the coil size (end to end dimension of polymer molecule), R_f, calculated from the Flory Huggins theory, is shorter than the distance s between the grafting sites, mushroom like structure is obtained when distance becomes shorter than R_f, the chains are

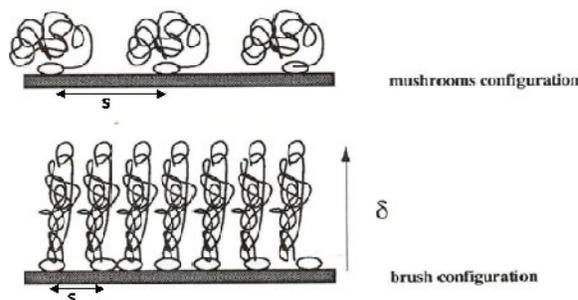forced to stretch in brush like configuration, Fig. 2 [24].

Fig. 2: A representation of conformation adopted by polymeric surfactant adsorbed onto the surface. From the top, the mushrooms/coils conformation is observed for $s > R_f$, brush conformation is found for $s < R_f$ i.e., for high density of adsorbing points, [24].

In the case of graft copolymers, the distance s between grafting sites is constant but in the case of adsorption distance, "s", is not constant and varies with respect to the external conditions of adsorption. The determination of the cross sectional area of polymer molecule and average separation between adjacent chains helps in interpreting the configuration of each polymer onto the surface.

Also the brush thickness δ can be calculated from the sum of N/ns (coils of size "s") from the following equation 3 [24].

$$\delta = \frac{N}{n_s} s = Na\left(\frac{a}{s}\right)^{2/3} \qquad (3)$$

and,

$$s = 2\left(\frac{\sigma_c}{\pi}\right)^{1/2} \qquad (4)$$

where "a" is the monomer size. The values of parameters were calculated using above equations according to Flory Huggins theory while Γ_m was taken from previous work of the authors [25-26]

Materials

Graphitic carbon black (Monarch 1000 jet black in colour, diameter of 12nm), selected as a model of carbon nanotubes, was kindly supplied by Cabot Chemical Corporation and had surface area of 300 m^2/g (measured by Nitrogen adsorption method) and 163 m^2/g (measured by Methylene blue adsorption method) and density of 1.8 g/cm^3 [25-28].

Table-1: Characteristics of dispersants for aqueous medium.

| Dispersant	Molecular Weight (kg/mol)	# of Ethylene oxide units	# of Propylene oxide units	Alkyl phenyl	Naphthol
PE/F 103	4.7	2 x 16	56	NO	NO
PE/F 108	16.2	2 x 148	56	NO	NO
Triton X100	0.65	10	----	YES (Octyl)	NO
Triton X405	1.9	40	----	YES (Octyl)	NO
NPE 1800	2.2	27	13	YES (Nonyl)	NO
Lugalvan BNO12	0.67	12	----	NO	YES

Deionized water was used for whole experimentation while decalin was supplied by Aldrich Chemicals and used without any further purification [25-28]. The concentration of carbon black in aqueous and non-aqueous medium was 8-22% (by weight).

PE/F 103, PE/F 108, NPE 1800, Triton X100, Triton X405, Lugalvan BNO12 were used for aqueous dispersions and Hypermer LP1, Hypermer B246 and OLOA 11000 were used for non aqueous dispersions by Yasin *et al*. [25-28]. The molecular weight, adsorption amounts and adsorbed layer thickness (calculated from rheology) for all polymers were used as reported by Yasin *et al*. [25-28]. Table-1 provides the characteristics of dispersants used for aqueous medium while Table-2 provides the information on adsorbed amounts of dispersants used in aqueous and non aqueous medium.

Table-2: Adsorbed amounts of dispersants for aqueous and non-aqueous media.

Dispersant	Amount adsorbed Γ_m ($\mu mol/m^2$)
PE/F 103	0.24 ± 0.02
PE/F 108	0.11 ± 0.01
Triton X100	4.4 ± 0.05
Triton X405	2.0 ± 0.05
NPE 1800	1.8 ± 0.05
Lugalvan BNO12	5.9 ± 0.10
Hypermer LP1	0.34+0.01
Hypermer B246	0.45+0.01
OLOA 11000	2.42+0.10

Hypermer LP1 (polyhydroxystearic acid), a homopolymer (molecular weight 2000 g/mol [29]), was supplied by Uniqema. Molecular formula of Polyhydroxystearic acid is given below, where n denotes the number of monomer units (hydroxystearic acid) and for Hypermer LP1, n = 7.
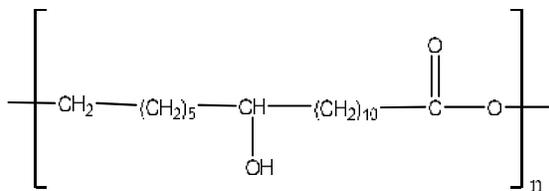
Hypermer B246 is a polyhydroxystearic acid/polyethylene oxide/polyhydroxystearic acid ABA block copolymer (molecular weight 5000 g/mol [30]) and was supplied by Croda Chemicals.

OLOA 11000 (polyisobutylene succinimide) has polar head group (polyamine) attached to a hydrocarbon chain (polyisobutylene) and both are connected by the succinimide group. It has molecular weight of 950 g/mol [31] and was supplied by Chevron Corporation. The molecular formula of OLOA 11000 is shown below, where n = 13 and m = 3 for the OLOA 11000.
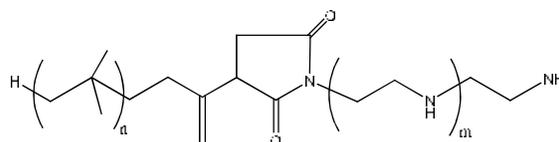
Scaling Analysis of Polymer Configuration

The cross sectional area σ_c, distance s and Flory radius R_f (calculated from equation 1-2) for all aqueous polymeric dispersants are shown in Table-3.

Table-3: The molecular cross sectional area, σ_c and distance, s, between adjacent chains for each polymer in aqueous medium and Flory radius calculated from equation 2.

Polymer	Area per PEO chain (σ_c) (nm^2)	Average separation per PEO chain (s)(nm)	Flory radius R_f (nm)
PE/F108	12.1	3.47	9.0
PE/F103	2.13	1.46	2.4
NPE1800	0.50	0.70	2.1
Triton X100	0.26	0.51	1.2
Triton X405	0.8	0.9	2.5
Lugalvan BNO12	0.22	0.47	1.3

The cross sectional area per PEO chain (nm2) is increasing with the size of stabilizing chain in comparison of Lugalvan BNO12 with PE/F 108. Triton X100 and Lugalvan BNO12 has the smaller stabilizing chains so occupying smaller cross sectional areas while PE/F108 have larger number of EO units and occupy a larger cross sectional area. This shows that how stabilizing chain regulates the adsorption amounts which is in line with the higher adsorption amounts (molar terms) in case of Lugalvan BNO12 with the smaller number of EO units (EO = 12) and PE/F 108 (EO = 296) showed lower adsorption amounts (Table 1-2) due to higher number of EO units. It is apparent from higher adsorption amounts that the anchor groups are tightly adsorbed onto the surface with smaller distance, s, and these tight anchor groups try to hold EO (hydrophilic chains) close together such that EO

chains may overlap with adjacent chains and hence extend further from the surface and thus occupy smaller cross sectional area. On other side PE/F 108 with larger number of EO units (EO = 296) (Table 1-2) adsorbs less on a molar basis and occupies higher cross sectional area but the adsorbed layer thickness was also higher in PE/F 108 (thickness was calculated from rheology by Yasin *et al*. [25-29]). That means the elongation of the stabilizing chain is a function of EO units and occurs both parallel to and perpendicular to the adsorbing surface and thus depends upon the ratio between distance s of adjacent chains and their thickness. Similarly, Triton X405 and PE/F 108 with a higher number of EO units showed higher molecular cross sectional areas than Triton X100 and PE/F 103 with lower number of EO units respectively. Hence the larger size stabilizing chains stops the tight packing of hydrophobic groups onto the surface and occupies larger area. So we may suggest that the size of stabilizing chain regulates the number of molecules adsorbed onto the surface as mentioned earlier.

Also by comparing the Flory radius, R_f, given in Table-3 with the distance s between grafting sites helps in interpreting the conformation of polymer molecule. If the Flory radius (end to end distance of polymer molecule), R_f, calculated by Flory Huggins theory, is shorter than the distance s between grafting sites, a mushroom like structure is obtained when distance becomes shorter than R_f, the chains are forced to stretch into a brush like configuration (Fig. 2). The Flory radius for all polymers is greater than distance "s" so we can suggest brush conformation of polymer molecule onto the adsorbing surface.

Table-4 gives information of cross sectional area σ_c, distance s and Flory radius R_f in case of non aqueous polymeric dispersants. Hypermer B246, is an ABA block copolymer of polyhydroxystearic acidpolyethylene oxide-polyhydroxystearic acid. Polyhydroxystearic acid is more soluble in decalin and xylene than polyethylene oxide so it may probably act as a stabilizing chain while polyethylene oxide adsorbs onto the surface. As polyethylene oxide does not dissolve in decalin so it adsorbs like PE/F 108 and whole polymer molecule adopts ABA configuration with two A's and one B (Fig. 1 (c)).

It can be seen from Table-4 that the Flory radius is longer than the distance s between grafting sites in the presence of Hypermer B246 and OLOA 11000 which shows that the polymer stabilising chains have brush configuration which is an indication of higher adsorption amounts (Table 1-2),

in molar terms, as compared to Hypermer LP1. While, Hypermer LP1 is more likely to adsorb on graphitic carbon black in loops and trains.

The area per PEO chain σ for each polymer and the distance s between adjacent chains (Table 3-4), and the experimentally determined adsorbed layer thickness δ (mean value of thickness determined from steady shear, oscillatory and AFM by Yasin *et al*. [25-28] are reported in Table-5. The measurement of true value of adsorbed layer thickness for PE/F 103 was not possible by rheology and AFM due to strong flocculation while value for PE/F 108 was obtained from AFM has been reported by the authors [25-28]. Table-5 shows dimensions of the adsorbed polymer on carbon black in water and concentration of EO units in the adsorbed layer. The adsorbed layer thickness from rheology and AFM experiments (Table-5) was larger than the average distance s (square root of the cross sectional area σc of one PEO chain, reported in Table-3) between the adjacent chains so the possibility of mushroom conformation can be excluded and we can assume the brush like conformation where chains are stretched out and can be described in terms of linear sequence of blobs (number of coils) of size s consisting of number of monomer units (ns). The brush thickness δ can be calculated from the sum of N/ns (coils of size s) from the equation 3-4 [24]. The values of σ and δ reported in Table-5 show that the increase of EO units generates the extension of the adsorbed polymer layer in both x-y axis i.e., both perpendicular to and parallel to the surface.

For example, by assuming a cylindrical shape of one adsorbed molecule on the basis of a brush like conformation of polymer chains, the molecule can be divided into number of coils or 'blobs' of diameter s equal to that of the cylinder. Each coil contains a number of monomer units of size a (Fig. 3) [32].
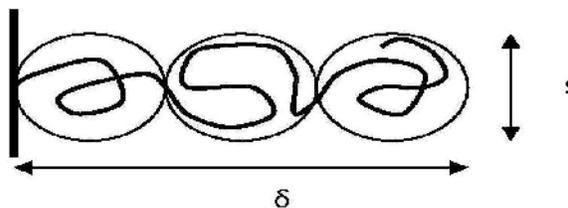

Fig. 3: Schematic representation of adsorbed polymer in the brush conformation comprised of 3 'blobs'. δ is adsorbed polymer layer thickness and $s = 2\left(\dfrac{\sigma_c}{\pi}\right)^{\frac{1}{2}}$.

Table-4: The molecular cross sectional area, distance s between adjacent chains for each polymer in non aqueous media and Flory radius calculated from equation 1-2.

Polymer	Area per stabilizing chain (Decalin) (σ) (nm^2)	Area per stabilizing chain (Xylene) (σ) (nm^2)	Average separation (Decalin) (s) (nm)	Average separation (Xylene) (s) (nm)	Flory radius R_f (nm)
Hypermer LP1	5.4	4.8	2.3	2.1	6.0
Hypermer B246	2.7	3.0	1.6	1.7	8.0
OLOA 11000	0.4	0.38	0.63	0.62	2.3

Table-5: Dimensions of the adsorbed polymer on carbon black in water and concentration of EO units in the adsorbed layer.

nEO/ $\sigma\delta$(nm^{-3})		4.0	--	14.0	11.0	12.0	15.0
n_{blobs} $\sqrt{(\pi/\sigma)}(\delta/2)$		1.5	--	4.8	6.4	4.0	7.0
Adsorbed layer thickness (nm)	Average	5.8	---	3.8	3.7	4.1	3.7
	AFM	5.8	---	4.5	4.0	5.0	5.0
	Oscillatory Test	---	---	3.5	3.5	3.6	3.0
	Steady Shear Test	---	---	3.6	3.6	3.7	3.1
Average separation per PEO chain (s) (nm)		3.47	1.46	0.70	0.51	0.9	0.47
Area per PEO chain(σ) (nm^2)		12.1	2.13	0.50	0.26	0.8	0.22
Polymer		PE/F108	PE/F103	NPE1800	Triton X100	Triton X405	Lugalvan BNO12

Table-6: Dimensions of the adsorbed polymer on carbon black in decalin and concentration of stabilizing units (polyhydroxystearic acid in Hypermer LP1 and Hypermer B246 and polyisobutylene in OLOA 11000) in the adsorbed layer.

$n_{stabilising\ units}$/ $\sigma\delta$ (nm^{-3})		---	2.0	8.0
n_{blobs} $\sqrt{(\pi/\sigma)}(\delta/2)$		---	2.0	5.0
Adsorbed layer thickness (nm)	Average	---	3.4	3.8
	AFM	---	3.0	4.0
	Oscillatory Test	---	3.6	3.5
	Steady Shear Test	---	3.6	3.7
Average separation per PEO chain (s) (nm)		2.3	1.6	0.63
Area per PEO chain (σ) (nm^2)		5.4	2.7	0.4
Polymer		Hypermer LP1	Hypermer B246	OLOA 11000

The blobs are extended perpendicular to the surface and their configuration (more or less extended brush like) depends upon the ratio of height δ and diameter s. So the ratio of δ/s will define the number of blobs which make up the chain and is approximately constant for each polymer as reported in Table-5 and from the constancy of coils, we may envisage that the conformation of each adsorbed molecule depends upon the structure of the molecule rather than its molecular weight. In Table-5 are also reported the density of ethylene oxide (EO) units which is the mean concentration of EO units in the adsorbed polymer layers. It is noteworthy that EO density per unit volume, nEO/$\sigma\delta$, is almost constant for each dispersant/polymer apart from PE/F 108 which is not a good stabilizer and is independent of polymer molecular weight, therefore volume V = $\sigma\delta$ is directly proportional to N (number of EO units). Again the constancy of density gives an evidence of the dependence of conformation of stabilizing chain on the structure rather than molecular weight. The difference in nblobs and density for PE/F 108 reveals a different structure with two distinct chains of PEO for each molecule.

In Table-6, again the density and the axial ratio (number of coils) is not constant for Hypermer B246 and OLOA 11000 (actually it is harder to compare Hypermer B246 and OLOA 11000 due to entirely different stabilising chain and anchoring chain in both dispersants) which shows the dependence of conformation of stabilizing chain upon the structure of molecule where former is a diblock copolymer with two stabilizing chains of polyhydroxystearic acid while OLOA 11000 is AB block with one stabilizing chain of polyisobutylene.

Conclusion

From the constancy of number of blobs and density for each polymer except PE series and Hypermer LP1, we can conclude that the conformation of stabilizing chain (PEO which provides a steric barrier) perpendicular to the carbon surface depends upon the ratio between the distance of adjacent polymer chains and their thickness. Also the elongation depends upon the structure of molecule rather than molecular weight. As structure is different in PE/F 108 (ABA block copolymer with two chains of EO units) and Hypermer LP1 (homopolymer) so they depicted the different density and n blobs. The experimentally determined adsorbed layer thickness from rheology and AFM measurements is greater than the distance between

anchoring sites so an elongated brush like configuration can be assumed according to the scaling theory.

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