POLYDISPERSITY OF POLYMER SURFACES USING SINGLE MOLECULE ATOMIC FORCE MICROSCOPY

by

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Abstract

Studying grafted polymers at surfaces using single molecule atomic force microscopy technique (AFM) was accompanied by investigation of those surfaces using well known surface characterization techniques. Chapter 1 summarizes two techniques used to characterize grafted polymer surfaces: contact angle measurements for interfacial energies and ellipsometry for the thickness of the attached polymers. The first chapter also illustrates difficulties or unexpected outcomes that could be encountered using these techniques. For example, ellipsometry data for grafted Poly (methyl methacrylate) (PMMA) monolayer were more complex than for other polymer monolayers studied in this work. This requires a modification of a simpler model which assumes a constant refractive index of a polymer (as in the bulk) all across the surface. The lateral inhomogeinity of monolayer properties as mentioned by Zografi *et. al.* [1] is considered.

Chapter 2 focuses on the study of the poly (dimethyl siloxane) (PDMS) grafted at silicon surfaces using the single molecule AFM technique. This study shows that entropy of mixing (ΔS_{mix}) plays an important role for determining the distribution of chain lengths grafted to the surface in polydisperse polymer samples [2-4]. This concentration dependent polydispersity is detected by measuring the polymer contour lengths from AFM measurements observed at surfaces at different volume ratios (different grafting concentrations). The data also shows that AFM data can correlate well to Gel Permeation Chromatography (GPC) at low concentration when there is an excess of reactive sites, therefore,

more representative of the excess number sites in solution. This result is encouraging, keeping in mind that single molecule AFM could be used as a direct surface analytical technique for polydispersity of polymers grafted at surfaces.

Chapter 3 focuses on the study of polystyrene grafted on gold surfaces. Two molecular weights were studied and both correlated to the GPC data. Here when grafting concentrations are high, persistence lengths obtained when fitting chain extension to the worm like chain (WLC) model are noted to deviate from those corresponding to single molecules. The force plot data indicate multiple ruptures of more molecules attached at the AFM tip. Higher interfacial tensions between the tip and polymer lead to higher rupture forces of the polymer from the tip.

Chapter 4 focuses on a study of PMMA polymer grafted on gold surfaces. Comparisons are made with PDMS. PDMS is known to be a very flexible polymer with an energy barrier of rotation of approximately zero [5]. However, as early as 1946, D. J. Crisp [6] observed that steric factors cause the PMMA monolayers to be patchy at surfaces. Sundarajan and Flory [7] later noted that the extent of steric hindrance caused by substituents of PMMA, CO-$COCH_3$ and CH_3, depends on size, shape and the planarity of the ester group. Sundarajan and Flory [7] also calculated energies of conformations for PMMA and predicted stabilities of g^- to be inexcessible and their data [7] showed most stable configurations to be all-trans class for both isotactic and syndiotactic PMMA chains (Figure 1). The isotactic conformation of lowest energy, $t_-/t_+t_-/t_+$ closely corresponds to a 10/1 helix [7].

Due to this purely steric factor strong interactions between PMMA polymer chains have been reported [8] to form double or single helices or form a stereocomplex [9] depending on ratios of tacticity.

As stated earlier AFM data on PMMA is more complex than that of PDMS or polystyrene and cannot simply be fit with the WLC model. To simplify the force plot data statistically, force plots are categorized into three groups depending on the shape or type of pulling events observed as will be shown in Chapter 4. To reduce the effect of interacting PMMA molecules, surfaces were prepared at gradually decreasing grafting concentrations. Also co-grafting of PMMA with short alkanethiols was used to try and isolate single PMMA molecules on the surface. About 20% of the force plot data were of 'sawtooth' type (mainly two ruptures) observed in higher as well as lower grafting concentrations. Persistence lengths for this set of data fit by the single molecule WLC (Worm Like Chain) model ('sawtooth') show a binomial distribution, indicating picking of one or two chains. This result indicates that the effect of interacting molecules could not be removed at these reduced grafting concentrations. These type of forceplots are observed in two different molecular weights 9K and 30K. The single molecule PMMA AFM data exhibit shorter contour lengths than GPC. However, dividing the contour lengths to the extension ratio brings the results of the two methods into closer agreement.

Chapter 5 compares surfaces and polymers discussed in earlier chapters.