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Polymer Concentration Profile near a Liquid–Solid Interface: Evanescent Wave Ellipsometry Study

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ABSTRACT: The phase retardation angle, $\Delta\Phi$, as a function of the incident angle was measured to study adsorption and depletion of polymers near a solid substrate from a solution by use of an evanescent wave ellipsometry technique. A lightly sulfonated ionomer dissolved in a polar solvent displayed an appreciable interfacial adsorption layer, while the nonionic precursor in ethyl acetate exhibits a depleted concentration profile. The results are in good agreement with adsorption or depletion layer profiles obtained previously by other techniques, i.e., X-ray fluorescence for polymer adsorption and optical fluorescence evanesent wave technique for depletion.

Introduction

It is widely known that ellipsometry[1] is very useful in the determination of film thickness at air–solid interfaces. However, the lack of sensitivity of conventional ellipsometry has limited its usefulness with regard to a variety of technologically interesting interfaces such as at liquid–solid interfaces where either polymer adsorption or depletion can occur. A recent report[2] shows that a phase-modulated instrument similar to the one used in this study has sufficient sensitivity to probe the phase transition of even a submonolayer of surfactants. The present work is devoted to a dilute macromolecular solution in the vicinity of an impenetrable wall. Such a system, for example, mimics the important role polymer materials play in the stabilization of colloidal particles. It is well-known that the stability of colloidal dispersions[3] depends on a variety of parameters such as polymer composition, molecular weight, solvent quality, and ionic strength. Therefore it is of interest to probe the polymer adsorption or depletion phonomena in terms of these variables.

As previously noted, the central problem in understanding the stabilization mechanism of colloidal particles by macromolecules is related to the detailed structure of the polymer near the liquid–solid interface. For this purpose, a very sensitive phase-modulated ellipsometer is utilized in order to examine whether it possesses sufficient sensitivity to monitor polymer adsorption or depletion at a liquid–solid interface. The initial measurements are compared with previous experimental results obtained from X-ray fluorescence[4] and fluorescence optical evanesent techniques[5] for polymer adsorption and depletion, respectively.

Experimental Section

The optical technique described in this report utilizes the total internal reflection at an interface located between an optically dense medium and a lean one. When there exists an interfacial layer of different optical property, i.e., either enhancement or depletion of the polymer concentration at the boundary in the present situation, the optical phase difference ($\Delta\Phi$) of the p-wave and s-wave reflection varies with the incident angle due to the change of the penetration depth of the evanescent wave. Thus, by measuring the phase difference as a function of the incident angle, one learns about the structure of the interfacial layers. If the thickness of the interfacial layer is small compared to the optical wavelength, then the critical angle of the total internal reflection (θ_t) is determined solely by the dielectric constant ($\epsilon = n^2$) of the bulk phases forming the interfaces. Following the derivation of Drude,[6] the phase difference at an incident angle (θ) is given by

$$\Delta\Phi(\theta) = 2k_0 \cos\theta \, \frac{(\epsilon_2)^{1/2}\epsilon_1 \sin^2\theta}{(\epsilon_2 - \epsilon_1)(\epsilon_2 \sin^2\theta - \epsilon_1 \cos^2\theta)}\, \eta \qquad (1)$$

where

$$\eta = \int_0^\infty \frac{1}{\epsilon(z)}[\epsilon_2 - \epsilon(z)][\epsilon(z) - \epsilon_1]\, dz$$

where $k_0 = 2\pi/\lambda$, λ is the wavelength of laser beam in vacuum, and ϵ_2, ϵ_1, and $\epsilon(z)$ are the dielectric constants of the dense, lean, and interface region at a distance z from the interface, respectively. At the critical angle (θ_t), eq 1 becomes

$$\Delta\Phi(\theta_t) = \frac{2k_0}{(\epsilon_2 - \epsilon_1)^{1/2}} \int_0^\infty \frac{1}{\epsilon(z)}\, [\epsilon_2 - \epsilon(z)][\epsilon(z) - \epsilon_1]\, dz \qquad (2)$$

The sign of $\Delta\Phi(\theta_t)$ gives a qualitative description of whether the interfacial layer is best described as an adsorbed (positive)

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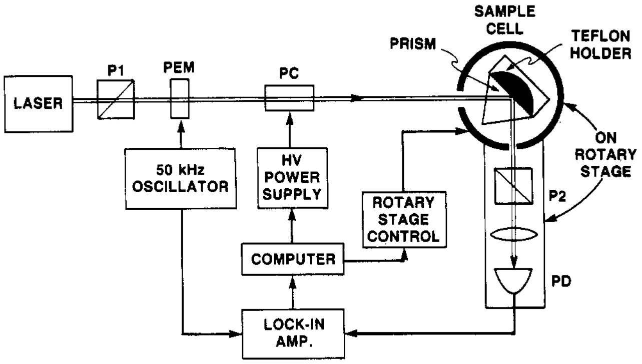

Figure 1. Schematic picture of the experimental apparatus. P_1 and P_2 are polarizers, PEM is a photoelastic modulator, PC is a pockell cell, and PD is a photodiode.

or a depletion layer (negative). A quantitative calculation of the phase difference as a function of the incident angle can be done with the Jones wave propagational matrix,[7] assuming a specific polymer concentration profile. The dielectric content $\epsilon(z)$ is related with the polymer concentration profile $\phi(z)$, such as

$$\epsilon(z) = \epsilon_{\text{solvent}} + \frac{\phi(z)}{\phi_b}(\epsilon_{\text{soln}} - \epsilon_{\text{solvent}}) \tag{3}$$

where ϕ_b is the polymer concentration in the solution and $\phi(z)$ is the polymer concentration at the distance z from the interface. Equation 3 was derived by assuming that the dielectric constant, ϵ, is linearly dependent on the polymer concentration.

The experimental arrangement is shown in Figure 1. A 0.5-mW He–Ne laser beam, operating at λ = 6328 Å, was used as the source. This instrument has been described in detail in a previous publication.[8] The sample cell was, however, designed to have the polymer solution injected without disturbing the optical configuration of the apparatus. Initially, an angular scan of phase retardation for the pure solvent was performed. This residual phase retardation from the pure solvent was to be subtracted from the phase retardation data of the polymer solutions. We found that the residual phase retardation was about 0.1 rad, which came mainly from the strain in the prism. It was important not to introduce additional strain in the prism when the polymer solution was introduced. With extreme care, the phase retardation due to exchanging the solvent with the polymer solution can be minimized to less than 0.5 mrad. The incident angle was varied from below to above θ_t. The angular resolution of the incident beam was better than 0.1 mrad. The overall sensitivity of the instrument for the phase retardation measurements was 0.1 mrad. The prism surface structure was modified chemically by grafting a monolayer of trichlorooctadecylsilane, using a procedure described by Sagiv.[9]

Anionically polymerized polystyrene was purchased from Polymer Laboratories, Ltd. The molecular weight of the polymer was 100 000 g mol^{-1} as determined by gel permeation chromatography. The preparation of the neutralized sulfonated polystyrene ionomer was similar to that described previously.[10] Polystyrene, 18.0 g, was dissolved in 240 mL of 1,2-dichloroethane (1,2-DCE) at 25 °C (i.e., polymer concentration was 7.5 g/dL). The solution was then heated to 50 °C, and the appropriate amount of acetyl sulfate was added, in this instance, 2.25 mL of acetic anhydride and 0.9 mL of concentrated sulfuric acid. The solution was continually stirred for 60 min at 50 °C, and the reaction was terminated and all free acids neutralized with the addition of 4.2 g of manganese(II) acetate dissolved in a mixture of 16.2 cm^3 of methanol and 0.9 cm^3 of water. It is noted that the free acid copolymer is completely soluble in 1,2-DCE, while marked turbidity change occurs with the addition of the manganese acetate solution. The polymer was subsequently filtered and the manganese neutralized ionomer (Mn-SPS) isolated by steam stripping. This latter process lasted 60 min. The sulfonated polymer was vacuum dried for 24 h at 100 °C. Sulfur content was determined by Dietert sulfur analysis and was used to calculate the sulfonation level. In this specific procedure, the sulfonate content was 8.3 mol % (2.31 wt % sulfur). The ratio of acetate to sulfonic acid in the neutralization scheme was 2.5 mequiv/mmol. Dimethyl sulfoxide (DMSO) solutions containing the above-described ionomer were prepared at room temperature with a conventional magnetic stirring apparatus. In all instances clear, gel-free solutions were obtained after 30–60 min under these mild agitation conditions. For the polymer adsorption phenomena, we have studied the interfacial concentration profile of the above-described ionomer (Mn-SPS) solution and compared these results with previous X-ray fluorescence measurements.[4] The polymer concentration was 1.0 g/dL. Similar procedure was used to prepare the unfunctionalized polystyrene (100 000 g mol^{-1})–ethyl acetate solution. Again the polymer concentration was 1.0 g/dL. This solution was used to study the depletion layer phenomenon. The polymer concentration profile at the liquid–solid interface obtained via our evanescent wave ellipsometry was compared with that obtained from previous optical fluorescence measurements.[5]

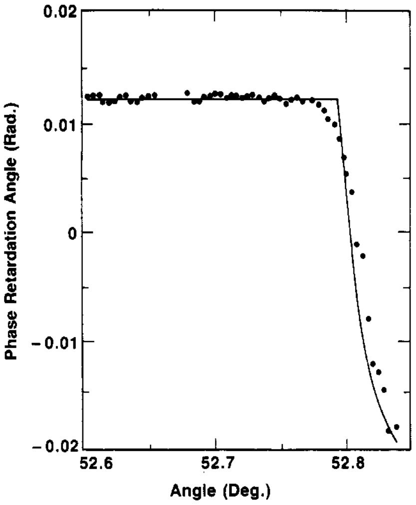

Figure 2. Phase retardation $\Delta\Phi$ as a function of incident angle. The solid dots are the experimental data and the solid curve is the theoretical data fitting. The polymer is 8.3 mol % mangnanese-neutralized sulfonated polystyrene (M_w = 100 000 g mol^{-1}) in dimethyl sulfoxide. The polymer concentration is 1.0 g/dL.

Results and Discussion

For polymer adsorption (i.e., Mn-SPS in DMSO), the analytical form[11–13] of the concentration profile is given by

$$\Phi(z)/\Phi_b = \coth^2(z/R + \sigma) \tag{4}$$

where Φ_b is the bulk concentration, R is the characteristic length, and $1/\sigma$ is the polymer concentration enhancement factor at the surface. In our analysis of the experimental data, this function was used to calculate the phase retardation $\Delta\Phi$. The results are presented in Figure 2 together with the experimental data; the theoretical fit to the data was obtained by using R and σ in eq 4 as adjustable parameters. It is satisfying to note that the characteristic length of $R \simeq$ 310 Å deduced from the fit is in excellent agreement with that obtained from the X-ray (synchrotron) fluorescence measurements on the identical polymer solution system.[4] In addition, the surface concentration parameter, $\sigma \simeq 0.1$, deduced from our measurements was also identical with that previously measured.[4] This means that the first layer from the interface is a 100% polymer layer. The estimated experimental errors are ±10 Å for R and ±0.01 for σ. This is a significant improvement over the X-ray data. Finally, the refractive index of the solution ($n = \epsilon^{1/2}$) obtained from the critical angle measurement was 1.473, which is slightly different from the literature value, due to the small amount of water absorbed in the highly polar solvent upon exposure to the atmosphere.

The polymer concentration profile function for a depletion layer (i.e., polystyrene in ethyl acetate) has the form[5,14,15]

$$\Phi(z)/\Phi_b = \tanh^2(z/R) \tag{5}$$

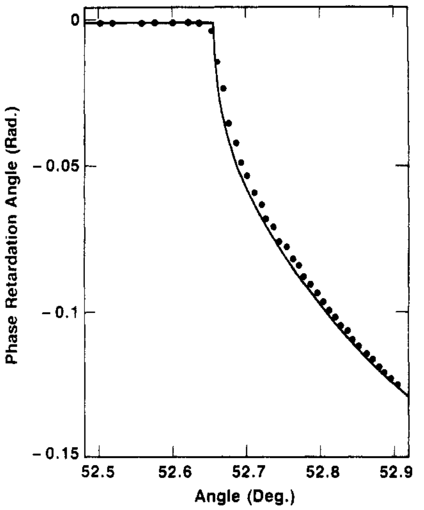

Figure 3. Phase retardation $\Delta\Phi$ as a function of incident angle for the depletion layer case. The solid dots are experimental data and the solid curve represents the theoretical data fitting. The polymer is polystyrene (M_w = 100 000 g mol^{-1}) in ethyl acetate, and the polymer concentration is 1.0 g/dL.

where Φ_b is the bulk concentration and R is again the characteristic length. This expression was used the analysis of the optical fluorescence measurements.[5] Figure 3 compares the experimental data (solid dots) with the theoretical curve (solid line). In this case, the signal level is low. This reduction in sensitivity is primarily due to the low contrast between the dielectric constants of the solvent and the depleted solution as predicted via eq 2. Even so, the characteristic length could be deduced and found to be approximately 70 Å. The previous optical fluorescence measurements yielded $R \simeq 47$ Å.[5] However, as anticipated, the error (±30 Å) in R is larger because of the smaller signal-to-noise ratio. The index of refraction of ethyl acetate obtained from the critical angle is 1.370 ± 0.001, which is in excellent agreement with the literature value of 1.370 at 20 °C.[16]

We note that the good agreement of the values of R and σ with previous determinations does not mean that eq 4 and 5 are unique functions describing the polymer concentration profiles. With the optical evanescent ellipsometry at λ = 6328 Å the minimum probing depth is d ($d \sim 400$ Å). It is then difficult to deduce from the measurements a unique functional dependence of the concentration profile on a length scale comparable to or less than d. In this respect, probes with smaller wavelengths have the advantage with X-ray or neutron sources, where the polymer concentration profile near an interface can in principle be determined more exactly.

It is interesting to compare the molecular dimensions of the two polymers with their corresponding experimental characteristic lengths. For the chain dimensions R_h of polystyrene in ethyl acetate, Schaefar et al.[18] have made extensive measurements of the diffusion constant D_0. They found that for the 10^5 g/mol sample, $D_0 \simeq 6 \times 10^{-7}$ cm^2/s, from which R_h was determined to be 85 Å, given that the viscosity of ethyl acetate is 0.426 cP. Therefore, the radius of gyration ($R_g \simeq 0.77R_h$) is roughly 65 Å. Our experimental result, $R \sim 70$ Å, is closer to R_g than R_h. In comparison to the result ($R \sim 47$ Å) obtained from the optical evanescent fluorescent technique,[5] our value of R seems to be more reasonable. Finally, an interesting question arises as to the characteristic length of the Mn-SPS ionomer in the polar solvent. Our previous viscosity and hydrodynamic radius measurements[19] of these dilute ionomer solutions show that the hydrodynamic radius is substantially higher than the molecular dimensions (R_h and R_g) of the neutral polymer precursor. Typically, these sulfonated polystyrene chains have a hydrodynamic radius of approximately 500 Å, with a corresponding radius of gyration of ~390 Å. This expansion is due to the dissociation of the metal counterions from the vicinity of the chain backbones (i.e., polyelectrolyte effect). The characteristic length ($R \sim 310$ Å) deduced from our experiment seems to correspond to the radius of gyration of the expanded Mn-SPS chain.

Conclusion

We have demonstrated the ability to measure adsorption and depletion profiles of polymers in solutions near a solid interface. As anticipated (from eq 1), the measurement of the depletion layer phenomena is substantially more difficult than for the adsorption layer. For a given polymer concentration profile, we have deduced the characteristic length and the surface concentration for the adsorption case and the characteristic length for the depletion case. The characteristic lengths for the adsorption case (Mn-SPS in DMSO) and the depletion case (PS in ethyl acetate) are close to the molecular dimensions of the polymer coils in a polar solvent and a good solvent, respectively. Therefore, it will be interesting to investigate the transition from depletion to adsorption by varying the amount of metal-neutralized sulfonate groups chemically bound to the polystyrene backbone or the treatment of solid substrates. It will also be interesting to study the dynamics of the adsorption (or depletion) process. These results will be addressed in a future publication.

Finally, it is important to note that the advantages of this technique as compared with other surface measurement techniques are (1) there is no need to chemically modify the polymer structure in order to enhance its X-ray or light fluorescence capability, (2) there is good penetration capability of optical waves through solid or liquid interfaces as long as the material is transparent, (3) the technique is nondestructive, and (4) measurements are easily performed in situ. However, this technique has a limited spatial resolution in determining the concentration profile because of the finite optical wavelength.

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Homopolygalacturonan Nitroxyl Amides: Matrix Deformation Induced Motional Perturbations of Cell Wall Polyuronides

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ABSTRACT: Galacturonic acid containing polymers in intact higher plant cortical cell walls were nitroxyl labeled at the C_6 position via an amide linkage in order to investigate the microscopic structure of the complex cell wall network in the dry and hydrated solid states. Cross-polarization and magic angle sample spinning NMR and EPR data indicate that the paramagnetic labels covalently attach near hydrophobic methyl ester domains, which, in turn, induce steric hindrance of the nitroxyl amide's motions. The energy of activation for internal motions of demethylated labeled cell wall powders was less than that of the native labeled matrix. Activation energies increased proportionally for these motions as a function of increasing the level of bound Ca^{2+}. EPR spectra of equilibrium-hydrated cell walls indicated that there were relatively large proportions of the galacturonosidic matrix in highly aggregated, possibly helical, domains due to steric and/or cross-linking effects occurring in the cell wall lattice. The fraction of weakly immobilized (isotropic) components, from composite EPR spectral envelopes at various levels of hydration, was obtained with pectin methyl esterase and alkali (solubilizes certain β-D-glucans and saponifies methyl esters) treated cell walls. The relative concentration of weakly immobilized EPR components was utilized as a measure of the interaction of the free sugar acid blocks with their surrounding polymer network. Enzymatically demethylated cell walls had an intermolecular coupling constant, derived from Fujita–Doolittle plots, 58% smaller than the native material, which provides strong evidence that methyl ester groups modulate segmental motion in the cell wall matrix via hydrophobic interactions. Divalent cationic cross-linkages between adjacent homopolygalacturonan blocks displayed a positively cooperative effect on an intermolecular coupling parameter as the fraction of binding sites being filled with Ca^{2+} increased. The latter observation argues that the binding of Ca^{2+} results in greater matrix deformation than can be explained by a random spatial distribution of the bound cations.

Introduction

The primary cell wall of most higher plants is believed to be a biphasic structure consisting of a skeleton of cellulose microfibrils held together by a rigid gellike lattice (the matrix polysaccharides).[1,2] The matrix components, which contribute about two-thirds to the total primary cell wall and middle lamellar mass, are polyhydroxy, hydrophilic, mostly carbohydrate macromolecules, which are extensively hydrated in vivo. Poly(galacturonic acid)-containing polymer species are one of the most important structural matrix polysaccharides in the stabilization of the wall lattice.[3,4] Little is understood about these sugar acid polymers' higher order structure[5] or how they form ordered arrays with a minimization of interaction energy in the native state.[6]

The associations of various polysaccharides in gels have been investigated,[7] and different types of interaction profiles between macromolecules can be distinguished. A gel structure has been proposed to exist through the exclusion of incompatible coils and the realignment of stiff structures with more compatible geometries to form mixed aggregates. However, the gel structure of polymer chains in cell wall matrices appears to be much more complicated because of the large manifold of weak forces interacting between the various matrix polysaccharides. In our laboratory, we have investigated[8] hydration-induced flexibility in a model system (e.g., poly(galacturonic acid), PGA) for the matrix components of higher plant cell walls. Thus, it is now possible to investigate more extensively the relative polymer flexibility of the sugar acid matrix components in the cell wall lattice as a function of various weak intermolecular forces. Such knowledge will assist in the elucidation of the higher order structure of certain cell wall polysaccharides in their native state as well as their physicochemical characteristics in the wall lattice.

The primary structure of cortical cell wall polymers of *Malus pumila* has been characterized in some detail.[9–12] The galacturonic acid containing matrix polymers exist in a form referred to as pectin or pectinic acid and are based on a backbone rich in α-(1→4)-linked D-galacturonic acid (the homopolygalacturonans) interspersed with (1→2)- and (1→2,4)-substituted L-rhamnose moieties, which are usually further linked with other neutral sugar polymers, forming "hairy" domains or side chains. The carboxyl groups of some of the galacturonan residues are methyl esterified to various degrees. Divalent cations have been shown to induce gelation in sugar acid macromolecules whereupon the ion–polyuronide lattice has been proposed to be represented as the "egg box" model as shown by circular dichroism[13,14] for solutions and by electron paramagnetic resonance[15] in intact higher plant cell wall matrices. Cell wall sugar acid domains have been found to contain up to 25–30% neutral sugars and 70–75% galacturonic acid monomer equivalents.[16] The high proportion of uronic acid residues is advantageous since our technique

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