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

M. W. Kim* and D. G. Peiffer
Exxon Research and Engineering Company, Route 22 East, Annandale, New Jersey 08801

W. Chen, H. Hsiung, Th. Rasing, and Y. R. Shen
Department of Physics, University of California, Berkeley, California 94720, and Center for Advanced Materials, LBL, Berkeley, California 94720. Received July 18, 1988; Revised Manuscript Received December 19, 1988

ABSTRACT: The phase retardation angle, Δφ, 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 adsorption layer, while the nonionic precursor in ethyl acetate exhibited a depleted concentration layer. The present situation, the optical phase difference, Δφ, is determined solely by the dielectric constant (ε) of the bulk phases forming the interfaces. Following the derivation of Drude, the phase difference at an incident angle (θ) is given by

\[ \Delta \phi(\theta) = \frac{k_0 \cos \theta}{(\varepsilon_2 - \varepsilon_1)^{1/2} \sin \theta} \left[ (\varepsilon_2 - \varepsilon_1)(\varepsilon_2 \sin^2 \theta - \varepsilon_1 \cos^2 \theta) \right] \eta \]  

where

\[ \eta = \int_0^\infty \frac{1}{\varepsilon(z)} \left[ \frac{1}{\varepsilon(z)} [\varepsilon(z) - \varepsilon_1] \right] \, dz \]

where \( k_0 = 2\pi/\lambda \), \( \lambda \) is the wavelength of laser beam in vacuum, and \( \varepsilon_2, \varepsilon_1, \) and \( \varepsilon(z) \) are the dielectric constants of the dense, lean, and interface region at a distance \( z \) from the interface, respectively. At the critical angle (θc), eq 1 becomes

\[ \Delta \phi(\theta_c) = \frac{2k_0}{(\varepsilon_2 - \varepsilon_1)^{1/2}} \int_0^\infty \frac{1}{\varepsilon(z)} \left[ \varepsilon(z) - \varepsilon_c \right] \,dz \]  

The sign of \( \Delta \phi(\theta_c) \) gives a qualitative description of whether the interfacial layer is best described as an adsorbed (positive...
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, assuming a specific polymer concentration profile. The dielectric content \( \varepsilon(z) \) is related with the polymer concentration profile \( \phi(z) \), such as

\[
\varepsilon(z) = \varepsilon_{\text{solvent}} + \frac{\phi(z)}{\varepsilon_{\text{bulk}} - \varepsilon_{\text{solvent}}}
\]

where \( \phi_b \) 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, \( \varepsilon \), 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 \( \lambda = 6328 \text{ Å} \), 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 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 80 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 solution of 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 % sulfurl). The ratio of acetate to sulfonic acid in the neutralization scheme was 2.5

The angular resolution of the incident beam was better than 0.1 mrad. The incident angle was varied from below to above \( \theta_b \). The overall sensitivity of the apparatus was \( \pm 0.01 \) mrad. The overall sensitivity of the apparatus was \( \pm 0.01 \) mrad. The overall sensitivity of the apparatus was \( \pm 0.01 \) mrad.

**Results and Discussion**

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

\[
\Phi(z)/\Phi_b = \coth^2 (z/R + \sigma)
\]

where \( \Phi_b \) 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 \( \sigma \) as adjustable parameters. It is satisfying to note that the characteristic length of \( R \approx 310 \text{ Å} \) 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, \( \sigma \approx 0.1 \) 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 \( \pm 10 \) Å for \( R \) and \( \pm 0.01 \) for \( \sigma \). This is a significant improvement over the X-ray data. Finally, the refractive index of the solution \( (n = 1.526) \) 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\(^5,14,15\)

\[
\Phi(z)/\Phi_b = \tanh^2 (z/R)
\]
where $\Phi_0$ is the bulk concentration and $R$ is again the characteristic length. This expression was used in the analysis of the optical fluorescence measurements. 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, Figure 3. Phase retardation theoretical curve (solid line). In this case, the signal level

is smaller because of the reduced signal-to-noise ratio. The index of refraction of water at $20^\circ$C is 1.370, $\Delta n = 0.001$, which is in excellent agreement with the literature value of 1.370 at $20^\circ$C.16

We note that the good agreement of the values of $R$ and $\sigma$ 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 $\lambda = 6328$ 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 $R_g$ of polystyrene in ethyl acetate, Schaefer et al.18 have made extensive measurements of the diffusion constant $D_w$. They found that for the $10^6$ g/mol sample, $D_w \approx 6 \times 10^{-7}$ cm$^2$/s, from which $R_g$ was determined to be 85 Å, given that the viscosity of ethyl acetate is 0.426 cP. Therefore, the radius of gyration ($R_g \approx 0.77R_w$) is roughly 65 Å. Our experimental result, $R \sim 70$ Å, is closer to $R_g$ than $R_w$. In comparison to the result ($R \sim 47$ Å) obtained from the optical evanescent fluorescent technique,3 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 polyvinyl alcohol. Our previous viscosity and hydrodynamic radius measurements19 of these dilute ionomer solutions show that the hydrodynamic radius is substantially higher than the molecular dimensions ($R_\sigma$ and $R_g$) of the neutral polymer precursor. Typically, these sulfonated poly(methyl methacrylate) chains have a hydrodynamic radius of approximately 500 Å, with a corresponding radius of gyration of $\sim 300$ Å. This expansion is due to the dissociation of the metal counterions from the vicinity of the chain backbones (i.e., ion-pair effect). The characteristic length ($R \sim 30$ 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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**References and Notes**

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

W. Chamulitrat and P. Irwin*  
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ABSTRACT: Galacturonic acid containing polymers in intact higher plant cortical cell walls were nitroxyl labeled at the C6 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 for these motions as a function of increasing the level of bound Ca2+. 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 alkaline (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 Ca2+ increased. The latter observation argues that the binding of Ca2+ 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 wall and middle lamellar mass, are polyhydroxy, structural matrix polysaccharides in the stabilization of acid polymers’ higher order structure or how they form extensively hydrated in vivo. Poly(galacturonic acid) containing polymer species are one of the most important in the native state. Gel structure has been proposed to exist through the wall lattice. The associations of various polysaccharides in gels have profiles between macromolecules can be distinguished. A philic, mostly carbohydrate macromolecules, which are the matrix polysaccharides. In our lab, we have investigated hydration-induced flexibility in a model system (e.g., polygalacturonic 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. 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 β-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, for solutions and by electron paramagnetic resonance 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. The high proportion of uronic acid residues is advantageous since our technique