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Analysis of Structure and Orientation of Adsorbed Polymers in Solution Subject to a Dynamic Shear Stress

Gregory Smith*, Shenda Baker (Harvey Mudd College),
and Chris Toprakcioglu (University of Patras)

Abstract

This is the final report of a three-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). Polymer-based separation techniques rely on the ability of a binding portion of the polymer to interact with a specific molecule in a solution flowing past the polymer. The location of the binding site within or out of the entangled polymer chains is thus crucial to the effectiveness of these methods. For this reason, the details of flow induced deformation of the polymer chains is important in such applications as exclusion chromatography, waste water treatment, ultrafiltration, enhanced oil recovery and microbial adhesion. Few techniques exist to examine the structure and orientation of polymeric materials, and even fewer to examine systems in a dynamic fluid flow. The goal of this project was to understand the molecular structure and orientation of adsorbed polymers with and without active binding ligands as a function of solvent shear rate, solvent power, polymer molecular weight, surface polymer coverage and heterogeneity of the surface polymer chains by neutron reflectometry in a newly designed shear cell. Geometrical effects on binding of molecules in the flow was also studied subject to the same parameters.

1. Background and Research Objectives

Understanding the details of flow-induced deformation of adsorbed and grafted polymer layers is especially important in applications such as size exclusion chromatography, adsorption and separation processes, waste water treatment, ultrafiltration, enhanced oil recovery and microbial adhesion. Typically, the polymers are adsorbed to spherical colloidal particles in a column to maximize exposed surface area. By flowing a solution through the

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column past the polymer with an active binding ligand attached (occasionally, the polymer itself has binding capabilities), a specific component in the fluid can bound to the polymer and separation can be achieved. Depending on the interactions between the polymers, surface and solvent, the polymer geometry will be closely packed to the surface, tightly intermingled among themselves or extending out into the solution. Thus, the binding site may be exposed to the solvent or hidden in the entangled polymer chains.

The effectiveness of these polymer-based separation techniques depends on the interaction of molecules in the fluid flow with these adsorbed polymers of a certain geometry. Polymer detachment is also a concern when using high shear rates to increase throughput and is difficult to measure directly. Furthermore, the effect of shear and extent of solvent interactions on the polymer geometry may be drastically different after the selected macromolecule has adsorbed to the polymer support [1]. As such, knowledge of the thickness, orientation, solvent and effect of shear rate on these polymer properties is imperative in the design of effective systems.

A number of techniques have been used to measure, in static equilibrium, the average adsorbed layer thickness, called the effective hydrodynamic thickness (EHT). However, only the hydrodynamic flow method [2] and the ellipsometric technique [3] have been used to examine the dynamic flow-induced deformation of adsorbed polymers. These techniques, though useful in obtaining an average polymer thickness, are unable to give information regarding the packing of the polymer, solvent interactions, or the location of the interactive end groups of the polymer in or out of the polymer "brush". Clearly, if the molecular portion of the polymer responsible for binding does not extend into the solution, any separation process will be thwarted.

These past experimental studies suggest that for low power solvents (weak polymer-solvent interaction), the EHT decreases with increasing shear rate until a limiting value, attributed to a stretching and ordered bending of the polymer close to the surface, is obtained. Usually, the EHT increases with increasing solvent power, but with increasing shear rate, this interaction is overcome by the deformation and elongation effects of the shear stress resulting again in a lowered EHT. Theories have predicted both EHT reduction [4] and swelling [5], depending on the shear rates and polymers used in the calculations. Clearly, the balance between the solvent power and the shear stress with respect to polymer geometry needs to be understood.

Neutron reflectometry provides a method by which the molecular system can be examined while subject to a shear stress. Because neutrons of the energies used in the reflectometry experiment can penetrate through quartz and silicon (up to 70% transmission through a 3 inch block), an enclosed shear cell with highly controlled shear rate parameters can

be used. The EHT can be obtained directly from the nuclear density profile. Additionally, the use of selective isotopic substitution will provide detailed information (to 5Å resolution) of the location of various parts of the polymer, solvent and/or adsorbed molecules relative to the surface. The techniques described in this project provide a means to examine a dynamic system that is not directly observable by any other technique. The interaction parameters of the solvent, surface and polymer necessary to design an effective system and to describe its physical parameters can thus be determined.

2. Importance to LANL's Science and Technology Base and National R&D Needs

One of the major challenges facing the nation is in the area of environmental clean-up. In addition to addressing questions of basic physical and chemical molecular interactions, this project applies to a number of systems used for environmental decontamination. First, separation of elements is often performed by liquid-phase polymer based retention techniques [6]. This is useful in removing and concentrating radioactive isotopes from large amounts of waste. In addition, miscibility of polymers in plastic recycling, protein separation by polymer based affinity chromatography and numerous other biologically based separation methods depend on the interactions of polymers, solvents and fluids. Development of new techniques or systems envisaged in this program furthers an initial development of the examination of fluids subject shear stress and will certainly introduce neutron scattering to a new and previously inaccessible community of researchers. This project supports Los Alamos core competencies in nuclear and advanced materials as well as earth and environmental systems.

3. Scientific Approach and Results to Date

The thrust of this project was to study the density profiles of polymers adsorbed to a solid/liquid interface, as a function of shear flow. To do this, we chose the technique of neutron reflectometry to examine the density profiles. In a previous study, we measured the polymer density profiles under static conditions [7, 8] using a quartz cell. By building on the design of the static cell, we designed a new type of shear cell for these studies [9]. This cell consisted of a polished single crystal quartz block sealed to a Teflon reservoir. The polymer/solvent solution to be studied was then put into the reservoir and a monolayer of polymer adsorbed from the solution onto the quartz surface. Then the remaining solution was flowed past the interface to produce a shear flow. Furthermore, we constructed a temperature

control box which provided a uniform and variable temperature environment for the cell and its contents.

As a model system for study, we chose a diblock copolymer consisting of poly(styrene) and poly(ethylene oxide) [PS-PEO]. These diblocks were adsorbed onto a quartz crystal from either toluene or cyclohexane. Either solvent is an extremely poor solvent for the PEO polymer so that these blocks will chemisorb strongly to the quartz forming an "anchor." By varying the anchor's molecular weight (MW) relative to the MW of PS we can control the effective grafting density. In turn, varying the relative sizes of the blocks permitted us to choose from closely spaced polymers which have an extended "brush" morphology [7] or sparsely spaced polymers which are characterized by a near-surface depletion layer and are referred to as "mushrooms" [8]. In addition, toluene is a good solvent and cyclohexane is a theta solvent ($T_\theta = 33^\circ \text{C}$) for PS. Thus, using various combinations of these polymers, solvents, temperature, and solvent flow rate, we could then examine the effects of shear flow on the polymer as a function of solvent quality, surface coverage and shear rate.

3.1 Shear Flow

The initial measurements were made on PS-PEO (MW PS=184,000 and MW PEO=7300) samples (0.05 mg/ml diblock in toluene). The static density profiles were well established [7] and so this gave us a known starting point. We found that at near surface shear rates up to 2500 s^{-1} (an average shear rate across the cell of approximately 400 s^{-1}), we saw no change in the reflectivity profile. We then changed the solvent from toluene to cyclohexane at room temperature. In this case, cyclohexane is a poor solvent. The sample was adsorbed from solution and the excess polymer was left in contact with the adsorbed monolayer. The measured static density profile was consistent with a polymer mushroom (Figure 1a). When the shear was applied at any rate between 300 and 2500 s^{-1} , there was a dramatic change in the density profile showing an elongation of the polymer layer thickness (Figure 1). This was the first time that the density profile of a polymer monolayer subject to shear has been measured with submolecular resolution [10, 11]. Also, it was found that the relaxation time for the system to return to its initial profile was on the order of days suggesting that entanglement of the PS chains are playing a role in the shear behavior. Since most theories of polymers subject to shear are for grafted polymers in a good solvent, we have modified our shear cell to reach shear rates roughly an order of magnitude higher than previously obtained so that we may see a change in the polymers in good solvent conditions as well as poor solvent conditions.

3.2 Solvent Quality Effects

Since we saw a dramatic change in the shear behavior with solvent quality, we undertook several experiments to understand the static effects of solvent quality on the density profiles of these adsorbed blocks. To do this, we did two sets of experiments. One in which

the polymer was adsorbed from cyclohexane at 45° C (above T_θ), then the solution containing polymer was replaced with a pure solvent (so that there would be no further absorption). Next, the reflectivity was measured as a function of temperature down to 20° C (below T_θ). At room temperature, a shear force was applied to the polymer as described above. While this data has not been fully analyzed, preliminary results suggest that the high temperature (above T_θ , where cyclohexane changes from being a poor solvent to a good solvent) profile is consistent with static absorption from toluene (also a good solvent) and that at low temperature the polymer collapses (as would be expected from a reduction in the radius of gyration upon change from a good to a poor solvent) and changes from a brush to a mushroom. We saw little change with shear at the low temperature. This suggests that the presence of excess polymer in solution plays a key role in the observed shear effects examined above. Finally, we exchanged the cyclohexane at room temperature with toluene. Again, the reflectivity profile was consistent with an instantaneous change in the polymer profile where the profile changes from a mushroom to a brush.

3.3 Concentration effects

Since we saw a change (noted above) in the shear behavior between having excess polymer in solution and having pure solvent next to the monolayer, we decided to study the effect of polymer concentration in solution on the static density profile. Three different solutions were prepared and put into the cell and permitted to adsorb for several days. The concentrations chosen were 0.0078 mg/ml, 0.0096 mg/ml, and 0.05 mg/ml of PS-PEO in cyclohexane. The density profiles were then measured for each case. Figure 2 shows the three profiles. While it is not clear why the polymer concentration should affect the ultimate surface coverage and profile, we do find a marked difference in the profiles of the polymer adsorbed from a poor solvent at different polymer concentrations.

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Fig. 1 The density profile of the (a) static and the (b) sheared diblock copolymer in a poor solvent.

Fig. 2 The neutron reflectivity data for three different polymer concentrations in cyclohexane. The surface coverage is increasing with concentration as indicated by the increasing depth of the first minimum.