Behavior of Adsorbed Polymer Layers in Shear and Elongational Flows

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ABSTRACT: New data are presented on apparent shear thickening of adsorbed layers and polymer solutions in various porous media of different geometries. We have observed that there is no apparent shear thickening if the pores are straight with smooth walls, i.e., in pure shear flow. Variations in cross-sectional area of channels or wall rugosities in straight pores are necessary to produce solvent flow perpendicular to the surface, i.e., a locally elongation flow. We advance the hypothesis that the apparent shear thickening is related to an elongational-flow-induced "coil stretch", a reversible transition of the adsorbed macromolecules, and rationalize this in light of previously published results.

Introduction

The conformation of adsorbed flexible polymers can be modified by the fluids flowing over them, thus changing the apparent rheological behavior of the fluids. This is what we term the "rheology" of adsorbed layers. Data on adsorbed layer thicknesses are frequently obtained by measuring the pressure drop–flow rate relation for flow of solvent over layer adsorbed on the walls of narrow flow channels (e.g., capillaries, membranes, porous media).[1-7] An intriguing feature of several sets of data of this type is that they exhibit, with increasing shear rate, an *increase* in the pressure drop, signaling an apparent *thickening* of the adsorbed layer.

Lee and Fuller[8] have measured ellipsometrically the average thickness of adsorbed layers of polystyrene absorbed on flat chromium mirrors in flowing systems under comparable shear rates to those where the apparent thickening has been observed. They found that under these conditions, the average layer thickness decreased with increasing shear rate, a result that is more intuitively understandable than thickening for flow over a flat surface. Cohen and Metzner[5] observed decreasing hydrodynamic layer thickness with increasing rate for flow of polystyrene solutions and of polyacrylamide solutions over adsorbed layers of each of these polymers, respectively. With solution flow, however, the question arises of the possible influence of interactions between the flowing polymers and the adsorbed polymers and whether this interaction could be modified by flow.

The question posed by this collection of results is the mechanism. Does an actual thickening of the adsorbed layer occur in a *simple shear flow* , or does some other hydrodynamic effect increase the frictional resistance of the layer? Most of the media in which thickening has been measured are not as smooth as chromium mirrors, so that the flow, instead of being a simple shearing flow, always has velocity components perpendicular to the surface, thus being locally elongational for the adsorbed macromolecules.

Two tentative explanations have been advanced previously for these observations. Fuller and Lee[9] speculated that the apparent thickening may be modeled by an adsorbed bead–spring model macromolecule with a conformation-dependent bead friction coefficient. In this model, as the macromolecule begins to extend (parallel to the surface, not perpendicular) under the action of the shearing flow, the frictional grip on the molecule by the flow tightens and, in turn, enhances the extension still further. This model gives the correct qualitative behavior but is unsatisfying in the sense that it does not explain why the shear-enhanced friction should be observed.

Gramain and Myard[3] proposed that inhomogeneous adsorption on the surface may produce a circulating velocity pattern, in regions of low adsorption, as though these act as cavities in the side of the flow channel. This circulation was speculated to push polymer segments perpendicular to and away from the wall. The argument against this is simply that there is very little evidence for the "spotty" adsorption they propose since measured adsorption density was relatively high (1.7 mg/m^2), implying high segment density in the adsorbed layer, and furthermore, very low segment density is needed to seriously impede solvent flow, so that it seems unlikely that significant circulation within the layer could occur.

A different explanation is proposed here. We will present the experimental evidence that *thickening does not occur with layers in straight pores with very smooth surfaces* such as with the chromium mirrors of Lee and Fuller.[8,9] Instead, it is observed exclusively in channels with some irregularity or nonuniformity in mean-cross-sectional area and in most porous media such as glass bead packs, sand packs, and sandstone. Such channels introduce both extensional straining components into the local velocity gradient tensor and velocity components perpendicular to the bounding surfaces, which can easily stretch macromolecules perpendicularly to the walls.

In the course of making our case for this explanation, we present new data on the flow behavior of adsorbed layers for both the aqueous-based hydrolyzed polyacrylamide (HPAM) system and for polystyrene (PS) in the organic solvent, cyclohexane.

Experimental Section

The basic flow apparatus has been described elsewhere.[10] It is very simple in design but capable of very high precision. Polymer solution is injected into the porous medium of interest with a syringe pump, guaranteeing constant flow rate. Flow is maintained during 1 day in order to ensure adsorption equilibrium. For studying solvent flow over adsorbed polymer, extensive washing at low flow rate during 1 day was performed to ensure complete removal of nonadsorbed polymer. The pressure drop associated with a certain flow rate is measured with a two-fluid U-tube manometer containing water–oil, water–mercury, or water–air, according to the magnitude of the pressure difference to be measured with an accuracy better than 2%.

Most of the measurements presented here are for flow through Nuclepore membranes made by track etching from either poly-

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carbonate or polyester materials. Both kinds of materials give reasonably uniform pore sizes. However, the polycarbonate membrane pores are considerably more regular, cylindrical, and straight than those in the polyester membranes. This fact is of particular significance in the results presented here. Electron micrographs and complete characterization of these membranes as distribution of pore sizes, shapes, and densities have been published by one of us and a different group of co-workers.[11]

For the experiments in aqueous media, the polycarbonate membranes were pretreated chemically by exposure for 50 min to a 10 wt% aqueous solution of ethylpyrrolidone in order to induce adsorption of HPAM. Pore radii (R_P) are determined from the pressure drop–flow rate relation for pure solvent in membranes never exposed to polymer, using the number density of pores determined via electron microscopy.

For the experiments with Nuclepore membranes, the apparatus contained membrane holders that permit stacking of up to 80 membranes in series separated by nylon grids. For experiments with other porous media a packed column was used in place of the membrane stack. For each porous medium/polymer solution combination, readings were obtained at several flow rates in the Newtonian flow regime and the mean value of apparent relative viscosity in the pore, η_r, is the one reported. Typical standard deviations are less than 3%. All solutions were well-filtered and degassed to prevent blockage by particules and air bubbles. Microgels were removed from solutions by a method previously reported in ref 10.

The results are always plotted either as apparent relative viscosity, η_r, versus nominal shear rate, with η_r being defined as the pressure drop measured for a certain situation divided by the pressure drop for pure solvent through that porous medium *with no adsorbed layer* or as apparent hydrodynamic layer thickness, L_H, derived by assuming Poiseuille in cylindrical capillaries and using the relation $\eta_r = (1 - L_H/R_P)^{-4}$. The nominal shear rates reported in the Nuclepore membranes are $\dot{\gamma} = 4Q/\pi\phi s(R_P - L_H)^3$ where Q is the flow rate, ϕ is the number density of pores, and s is the total membrane surface area exposed to the flow. The proper definition of the nominal shear rate for porous media more complicated than Nuclepore membranes is nontrivial and has been discussed by Chauveteau.[12] However, since we never attempt to establish an exact correspondence among shear rates for media of different structures, none of the results to be presented here depend on the precise definition used for the nominal shear rate.

In all cases, the walls of the porous medium are saturated with adsorbed polymer. In some cases, the pressure drop measurements, are for pure solvent flowing over the adsorbed layer; in other cases, they are for polymer solutions flowing over the adsorbed layers. This is a significant point since we shall demonstrate that there are interesting correspondences between the rheology of adsorbed layers and the rheology of flowing polymer solutions in porous media.

Two types of polymer were studied. The hydrolyzed polyacrylamide (HPAM) is a commercial product of Dow Chemical Co. known as Pusher 700 with a weight-average molecular weight of about 7.5×10^6 and a polydispersity of 2.2.[13] Approximately 30% of the acrylamide groups are hydrolyzed to acrylic acid, giving the material a significant polyelectrolyte character. For all experiments reported here polymer concentration was 320 ppm. HPAM was studied in aqueous solutions at 30 °C at pH 7 with a salinity of 20 g/L NaCl. These are good-solvent conditions for HPAM. The polystyrene (PS) samples used were linear, atactic research standards from Polysciences, Inc., of polydispersities less than 1.3 and weight-average molecular weights of 48×10^6, 30×10^6, 15×10^6, and 10×10^6, respectively. PS was studied near the Θ point in cyclohexane at 35 °C. In all of the experiments, it was checked to see whether there was any variation in adsorb layer thickness of polymer with either the duration of the experiment or after flow at high shear rates. In all our conditions, such effects were determined to be negligible, though they have been observed under other circumstances.[9]

Results

Figure 1 shows the data for HPAM flow through polycarbonate (PC) and polyester (PE) Nuclepore membranes, plotted as apparent relative viscosity versus nominal shear rate in the pore. The upper two curves a and b in both

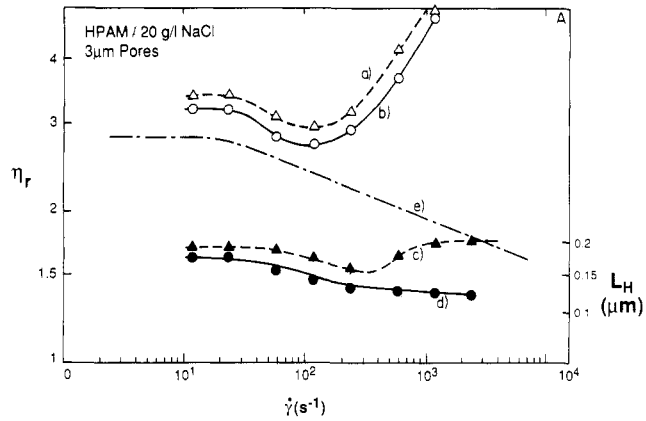

Figure 1. Data on hydrolyzed polyacrylamide (HPAM) in 3-μm-diameter Nuclepore membranes. (a) HPAM solution flow over HPAM adsorbed on walls of polyester membranes (see Figure 2); (b) HPAM solution flow over HPAM adsorbed on walls of polycarbonate membranes; (c) pure solvent flow over HPAM adsorbed on walls of polyester membranes; (d) pure solvent flow over HPAM adsorbed on walls of polycarbonate membranes; (e) relative viscosity versus shear rate for bulk solution (C_p = 320 ppm).

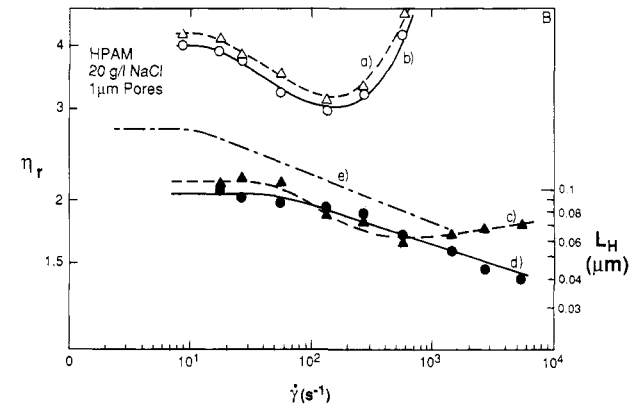

Figure 2. Data on HPAM in 1-μm-diameter Nuclepore membranes. Curves have same designations as in Figure 1.

Figure 1 and 2 are for polymer solution flow through the two kinds of membranes. The slightly higher apparent viscosity level for the PE membranes arises from either a slightly smaller pore radius or from differences in adsorption energy but the difference in adsorbed layer thickness on the two membranes is not significant. In all other respects, the two curves have similar shapes. They are both higher than the apparent relative viscosity measured in a conventional Couette viscometer (curve c). In the low shear rate, Newtonian plateau zone, where there is little deformation of the molecules, this higher apparent viscosity produced by the adsorbed layer (lower curves) can be translated directly into an apparent hydrodynamic thickness of the adsorbed layer. This is illustrated on the right-hand ordinate.

Several points must be raised with respect to the observed L_H values. The apparent, low shear rate hydrodynamic layer thicknesses for this polymer is different in the two membranes of different pore sizes. The radius of gyration (R_g) of this polymer is approximately 2000 Å, whereas L_H is about 1900 Å in the 3-μm pore (Figure 1) and 900 Å in the 1-μm pores (Figure 2). In the absence of good data on the adsorbed amounts within the pores, which are difficult to obtain and which we do not have, it is difficult to interpret this observation. We note that Idol and Anderson[6] observed also that L_H increases with R_P, whereas Gramain and Myard[3] found L_H independent

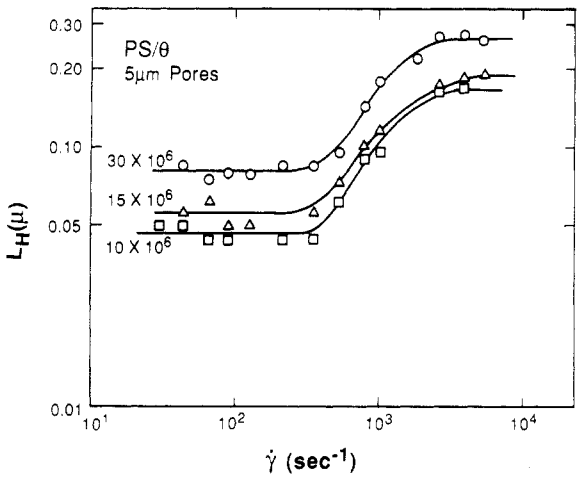

Figure 3. Data on solvent flow over polystyrene (PS) adsorbed layers in 5-μm polyester Nuclepore membranes. Data are plotted as apparent hydrodynamic layer thickness (in μm) versus nominal shear rate. Numbers indicate PS molecular weights.

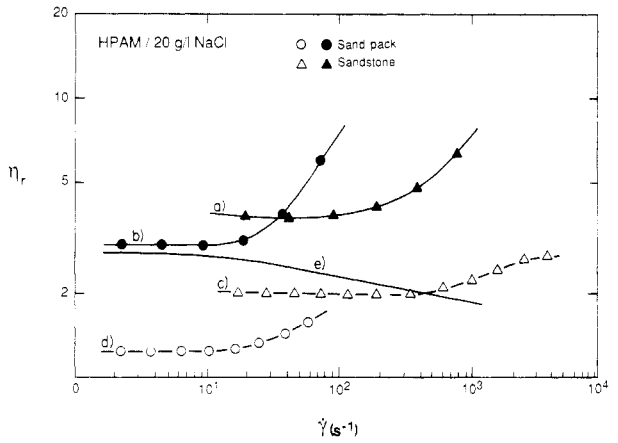

Figure 4. Data on HPAM in sandstone (curves a and c: $k = 18 \times 10^{-3}$ μm^2, $\phi = 6\%$, $2R_P = 7$ μm) and sand pack (curves b and d: $k = 4.5$ μm^2, $\phi = 38\%$, $2R_P = 20$ μm). (a and b) HPAM solution flow over HPAM adsorbed layers. (c and d) Pure solvent flow over HPAM adsorbed layers.

of R_P. Cohen[7] has suggested that these results may depend on the relative molecule and pore size.

On increasing the shear rate from the Newtonian zone, one observes, in the upper curves, first a slight, but reproducible, shear-thinning behavior, followed by a shear-thickening zone. The shear thinning sets in at approximately the same nominal shear rate($\dot{\gamma}^* \approx 20$ s^{-1}) as where shear thinning begins outside of the porous medium. At much higher shear rates ($\dot{\gamma}^{**} \approx 200$ s^{-1}), an abrupt shear thickening is observed. This pattern of behavior has been well-documented[2,10] when polymer solutions flow both in converging–diverging channels and in nonadsorbent porous media and has been shown to arise from elongational flow effects leading to a coil–stretch transition. Thus, shear thickening of a polymer solution is expected to come from entrance and exit effects for both PC and PE membranes, but an additional effect could come from adsorbed layer thickening in PE membranes. Elongation flow zones that arise in porous media may be divided qualitatively into two categories. One category is the convergent and divergent flow zones at pore entrances and exits. Such convergent and divergent flow zones exist at the faces of the membranes for both PE and PC membranes. The other situation giving rise to elongation flow zones is the blockage of flow due to obstacles or roughness in the channel. These create stagnation points around which flow is elongational, thus producing macromolecular elongation. Both sorts of elongational flow zones exist in the PE membranes, since the pore walls are rough.

The lower two curves (c and d) in Figures 1 and 2 are for solvent flow through pores in PC and PE membranes with polymer adsorbed on the pore walls. In contrast to polymer solution flow, we see a marked difference in behavior between PC and PE membranes. In the PC membranes, we observe only shear-thinning behavior if we expect a very slight effect in 3 μm (Figure 1), while in the PE membranes we observe also a net shear thickening at high shear rates (400–800 s^{-1}). We note here, without beginning the complete discussion, that the shear-thickening effects for the adsorbed layers are observed in the PE membranes, which have much rougher walls. Figure 3 illustrates similar results with PS in cyclohexane in the PE membranes only. (The PC membranes will not tolerate immersion in cyclohexane long enough to get reliable, stable measurements of the apparent viscosity.) The low shear rate L_H values here vary with the square root of the molecular weight as expected but, as in Figures 1 and 2, $L_H < R_g$ of the free polymer. The question of the absolute coefficient relating L_H to R_g has been discussed by Cohen.[7] There is no general agreement on what this ratio should be. We note that these organic polymer membranes are not expected to provide strong adsorption affinities as, for example, with the silica[11] or metallic surfaces[9,10] studied previously. Here, the data are more scattered but seem to exhibit no shear thinning, only a pronounced shear thickening above a threshold in shear rate at about 500 s^{-1}. the absence of observable shear thinning may be due either to the lower hydrodynamic layer thickness in this organic system than in the aqueous polyelectrolyte system or the absence of measurements at low enough shear rate. Moreover, the precision of the data in Figure 3 is poorer than in Figure 1 and so some small shear thinning may be undetectable.

The onset of shear thickening for PS layers in the PE membranes occurs at approximately the same stress as for HPAM layers in the PE membranes having large diameters, 3 and 5 μm. Furthermore, the onset shear rate is roughly independent of the molecular weight of the adsorbed polymer. This may indicate that the effect is related to the geometry of the porous medium, which is invariant in Figure 3. Alternatively, it could be that tails are elongated and that the size of tails does not depend on moecular weight. The observed thickening for PS is significantly much higher than for HPAM. This is thought to be related to differences in solvent quality, the adsorbed layer in a Θ solvent being more extensible. Another observation, very apparent in Figure 3 but also observable in Figure 1, is that, at high shear rates, the shear-thickening effect seems to saturate, showing it is not possible to elongate the adsorbed layer further under these circumstances, and complete reversibility of the curves shows there is no significant desorption at high flow rates.

Figures 4 and 5 show results for HPAM solution flow and flow of pure solvent over adsorbed HPAM layers, in more irregular porous media, namely, sand packs, a porous sandstone (Figure 4), and a glass bead pack (Figure 5). Here again, shear thickening is observed for both solution flow and for solvent flow over adsorbed layers. In this case, there is little or no observable shear thinning, possibly due to the more strongly elongational character of this flow than the flow in Nuclepore membranes. An observation that is significant is the correspondence that exists in the threshold shear rates for the onset of shear thickening for solution flow and for solvent flow. This will be dealt with in more detail in the discussion.

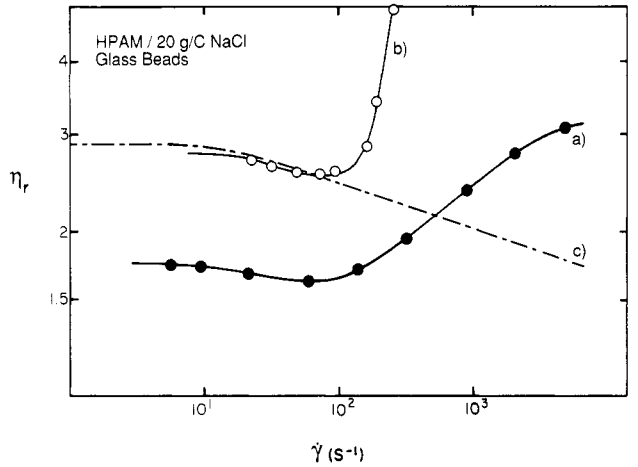

Figure 5. Data on HPAM adsorbed layers in glass bead packs. (a) $k = 0.66\ \mu m^2$, $\phi = 40\%$, $2R_P = 5.8\ \mu m$; bead diameter 20–28 μm. Data is for pure solvent flow over adsorbed layers. (b) Bead diameters 400–500 μm, $k = 137\ \mu m^2$. (c) Data for HPAM flow without adsorbed layer effect.

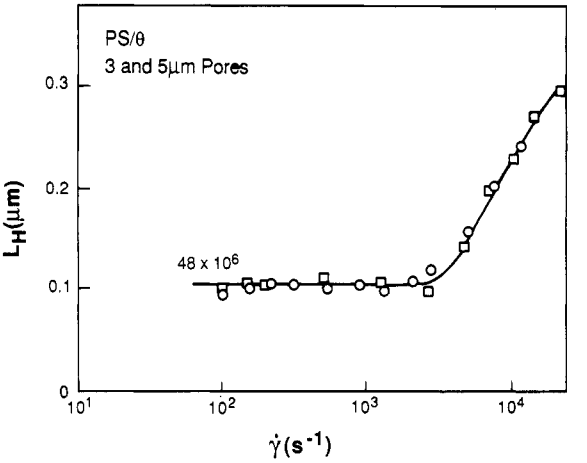

Figure 6. Data on solvent flow over PS adsorbed layers. PS molecular weight = 48×10^6. Two different R_P indicated. Data are plotted as apparent hydrodynamic layer thickness (in μm versus nominal shear rate).

Discussion

The principal observation we report here is that of the apparent shear-thickening behavior of adsorbed polymer layers in several different porous media where there exists some irregularity of the channel cross section (PE membranes) or in structure (bead packs, sand packs, and sandstone). In contrast, in narrow straight pores of very smooth walls and regular cross section (PC membranes), we observe no apparent shear thickening with the same adsorbed polymers.

We noted earlier that the hydrodynamic thickness is very similar for HPAM on PC and PE membranes, even if we observe that the adsorbed thickness of HPAM increases with pore size. We attribute, therefore, the major differences in behavior to the differences in geometry of the pores in the two types of membranes.

There are some subtler observations that one can make to elaborate on this picture. We note that the threshold shear rates for the observation of shear thickening in Figure 2 are different for solution flow and for solvent flow, whereas in Figure 4 the shear-thickening thresholds for solution and solvent flow are identical. In the Nuclepore membranes the major elongational flow zones are on the pore axis at the entrance and to a lesser extent at the exit of the pore. Elongation in these zones produces the apparent shear thickening for polymer solution flow, which is observed at the same shear rate in both PE and PC membranes. Adsorbed polymer, anchored to the pore wall, does not experience these zones if we except a zone near the pore exit due to probable but no sure adsorption of polymer on the sides of the membranes. Thus, there is no apparent thickening in the PC membranes. A very slight effect could be detected in Figure 2, possibly due to extension of adsorbed layer near the exit face. Elongation is produced in the PE membranes by flow over and around the irregularities of the pore wall. A higher flow rate is therefore required to see apparent thickening of the adsorbed layers.

On the other hand, in the irregular porous media studied in Figures 4 and 5, elongational flow zones exist not only in convergent–divergent regions as in PC membranes but also at stagnation points, for example, behind particles. It has been demonstrated experimentally by studying flow around well-defined assemblies of beads[10,14] that these stagnation zones induce macromolecular elongation at much smaller flow rates than convergent zones. A factor of 10 was found for the same HPAM sample in both pack and assembly of glass beads (see Figures 14 and 15 in ref 10). In any case, in these irregular porous media, in constrast to PC Nuclepore membranes, adsorbed polymers are located in elongational flow zones. Adsorbed polymer experiences a very similar elongational field to that experienced by flowing polymer. Thus, in this case, the threshold shear rates are the same. As expected, the threshold shear rate values depend strongly on geometrical shape which determines the elongational character of the flow near the surface.

Gramain and Myard[3] reached a different conclusion from their study of HPAM flow through Millipore filters of different sizes. They observed a shear-thickening behavior in membranes of different pore sizes that could be normalized by using $\dot{\gamma}R_P$ as the abcissa. They show plots similar to Figure 6 where, in contrast to our data, η_r was a common function of $\dot{\gamma}R_P$. Since $\dot{\gamma}R_P$ is a sort of average velocity in the pores, they concluded that *this* was the controlling parameter, not the velocity gradient. Such a normalization does not work at all for the data presented here. Figure 6 illustrates that $\dot{\gamma}$ is a good normalization parameter of our data for PS and PE membranes of two different pore sizes. This latter parameter, of course, scales all the components of the velocity gradient tensor, in particular the elongational ones due to the wall irregularities. The pertinent parameter is expected to be $\dot{\gamma}e$ for the cylindrical pores with rugosity of characteristic dimension e.

We believe, however, that there is a way to reconcile our observations with those of Gramain and Myard.[3] It rests on observations of the structure of the Millipore membranes used by Gramain and Myard. These are membranes composed of small fibers (diameter = $d_f \equiv 10.8\ \mu m$) of cellulosic material with a very high porosity (~80 to 90%). Different membrane pore sizes consist of the *same* small fundamental fiber diameter, d_f, with different structures leading to different pore diameters, d_p. The nominal shear rate Gramain and Myard use (Figure 6) is proportional to the average velocity of flow through the medium v, divided by d_p, i.e., $\dot{\gamma} = v/D_P$. The effective extensional velocity gradient $\dot{\epsilon}$, felt most strongly by the adsorbed macromolecules in the stagnation zones around an individual fiber, is proportional to v/d_f. Since d_f is constant with this series of membranes, v constant implies $\dot{\epsilon}$ constant. Our opinion is that $\dot{\epsilon}$ is the controlling parameter. Therefore, v normalized the Gramain–Myard data. There is no reason why it should normalize our data, however, since our geometry does not include a constant

length like D_f, but rugosity or particles of different sizes.

In summary, we feel that the apparent flow-induced shear thickening observed by us and by others is, in fact, an elongational-flow-induced "coil–stretch" transition of the adsorbed macromolecules. Rugosity of the pore walls or irregularities in pore structure are necessary to produce the local elongational flow. We do not, however, want to insist that we have proven this. Besio et al.[15] have recently published the first study of elongational flow effects on polymer adsorption. Our opinion is that this kind of work is essential for clarifying the hydrodynamic behavior of adsorbed polymer layers in the presence of rugosity.

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Self-Consistent Field Model of Polymer Adsorption: Matched Asymptotic Expansion Describing Tails

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ABSTRACT: General self-consistent field equations, derived previously, are solved within a perturbation scheme for the configuration probability of polymer chains. Building upon an earlier ground-state solution which describes adsorption in an "inner" region but precludes the prediction of tails, an "outer" region solution is developed herein as the lowest order term in a perturbation expansion of the configuration probability in powers of reciprocal chain length. This solution is asymptotically matched with the inner (ground state) solution, yielding a uniformly valid approximation. From this solution, we derive an analytical expression for the polymer volume fraction profile, including contributions due to segments contained in loops, tails, and nonadsorbed chains. Predictions for the adsorbed amount of polymer, ellipsometric layer thickness, and hydrodynamic layer thickness agree qualitatively with experimental data. We describe the variation of chain configuration statistics (e.g., the distribution of segments in trains, loops, and tails) with experimental parameters. These results are analyzed by using simple thermodynamic arguments.

Introduction

A considerable number of interesting and important materials and processes contain interfaces modified by a polymeric component. An extensive list of applications of this type, give by Eirich,[1] includes the stabilization and flocculation of colloidal suspensions. Such systems are dominated by interfacial effects; their stability and properties depend strongly upon the details of particle interactions, in this case mediated by adsorbed layers of polymer molecules. Naturally, an understanding of the interactions of adsorbed polymer layers requires a complete description of the configurations of the constituent molecules. This description is the object of most theories of polymer adsorption.

The earliest polymer adsorption theories consider isolated adsorbed molecules but have little practical relevance since even for weak adsorption energies, a large number of molecules may adsorb per unit area, resulting in significant intermolecule interaction. Nonetheless, valuable insights did emerge. For example, Hesselink[2] employed the random-walk formalism developed by Chandrasekhar[3] to calculate the number of possible configurations of isolated molecules attached to the surface by one or both end groups ("tails" and "loops", respectively). Idealizing a polymer molecule as a "chain" of "segments" exhibiting random-walk statistics, Hesselink found that a tail of n segments has $(2\pi n)^{-1/2}2^n$ possible configurations, while a loop of n segments may assume any of $(2\pi n)^{-1/2}2^n n^{-1}$ configurations. As Takahashi and Kawaguchi conclude in their review,[4] consideration of only configurational entropy implies that the existence of tails is favored over that of loops, especially for large n. This result contrasts sharply with many early and even some contemporary adsorption theories which (implicitly or explicitly) assume that polymer chains adsorb only in loops and "trains" (runs of adsorbed segments).

The most comprehensive and successful theory describing the random adsorption of homopolymers is the lattice model of Scheutjens and Fleer (SF). The SF theory, which has been described extensively,[5] treats a wide range of experimental conditions with no a priori assumptions about the configurations of adsorbed polymer chains. The predicted characteristics of the adsorbed layers agree qualitatively with much experimental data, but the model is limited in several respects. In particular, the SF model involves the discretization of space, necessitating the selection of a lattice geometry (i.e., simple cubic, hexagonal close packed, etc.) thay may not accurately reflect the

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