Adsorption and Desorption of Polystyrene from Dilute Solutions in Shear and Elongational Flow

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ABSTRACT: The influence of flow on the adsorption and desorption of high molecular weight polystyrene on chromium was studied by ellipsometry for two solution conditions, in decalin at 22 °C (a slightly good solvent) and in cyclohexane at 35 °C (a Θ solvent). Measurements of layer thickness, after collapse induced by solvent removal, provided adsorption levels (mass/area) in both shear ($0 < \dot{\gamma} < 1000\ s^{-1}$) and biaxial elongation ($0 < \dot{\epsilon} < 25\,000\ s^{-1}$). With decalin the different flow environments had little influence on either adsorption or desorption processes; with cyclohexane a greater impact was noted, although only during adsorption. It appears that flow only affects the adsorption level of a weakly attached subfraction of the bound-chain population.

I. Introduction

Adsorption of homopolymer chains from solution plays an important role in numerous commercial applications of soluble polymers, from colloidal stabilization to chromatography. Adsorption most often occurs by diffusion of dissolved chains to an attractive surface, where the attaching molecules adopt, at equilibrium, an average conformation similar to that of a bulk, quiescent solution. When the contacting solution is dilute and the binding forces are weak, the nondilute adsorbed surface layer is highly diffuse, extending into the solution about twice the polymer's mean radius of gyration. Recently, several groups have collected data that suggest that polymer adsorption can be significantly modified by external hydrodynamic or electrostatic forces.[1-4] The thickness and density of polymer layers adsorbed while subjected to these forces appear qualitatively different from those produced through static adsorption.

Only a few studies have focused on the influence that hydrodynamic forces might have on adsorption processes, mostly in well-developed, shear-dominated flows.[1,5,6] Gramain and Myard,[7] and later Cohen and Metzner,[8] examined polymer adsorption in filters and capillaries, respectively, media in which transient flows of combined shear and elongational character are created at a local scale. In both investigations the flow rate/pressure drop relationship through coated and uncoated media was determined and then, by comparison, an effective hydrodynamic thickness (EHT) calculated. The EHT is sensitive to both the density and spatial extent of adsorbed chains, particularly tail sections that protrude far into the solution. Cohen and Metzner found a decrease in EHT with increasing wall shear rate, contrary to the observations of Gramain and Myard. Subsequently, for a polymer system at Θ conditions, Cohen[9] observed an increasing and then a decreasing EHT as shear rate increased.

Lee and Fuller[1,5] conducted an extensive study of the effects of shear flow on the polymer adsorption kinetics over flat substrates and found that adsorption slowed down as the shear rate increased (shear rates were in the range of 0–2000 s^{-1}). However, the thickness of the layers, measured by in situ ellipsometry, did not change much due to the flow. Combining ellipsometric determinations of film thickness and refractive index, Lee and Fuller noted a significant decrease in the steady-state adsorption level when the shear rate exceeded a critical value; the critical value depended strongly on molecular weight. In a more recent paper McGlinn et al.[6] studied adsorption kinetics at lower shear rates ($\sim 3\ s^{-1}$) and concluded that the apparent adsorption level for an intermediate molecular weight polymer may not attain steady state in flow. Similar observations were reported by Barham and Keller[10-13] in a series of papers in which the phrase "adsorption-entanglement layer" was introduced to describe the accumulation of polymer near a surface exposed to flow. Chains in adsorption-entanglement layers may not be directly attached to the surface by short-range physical or chemical bonds, suggesting a multilayer adsorbed structure of the type observed with low molecular weight species.

Flows often possess combined shear and elongational character. Freely dissolved, flexible-chain molecules subject to elongation flows are believed to undergo a transition from a coiled to an extended state at certain critical flow conditions governed by the Deborah number *De*, defined as the product of the molecular relaxation time τ and the elongational rate $\dot{\epsilon}$. The sole direct investigation of elongational flow's effect on polymer adsorption was conducted with an impinging jet flow. Curious patterns were sometimes noted on the dried substrate, consisting of concentric rings centered at the stagnation point (a "bulls-eye"). A connection between the rings and conformational rearrangements in the Θ solution was suggested by the authors. Bagassi et al.[14] also discussed the role of elongational flow on adsorption and adsorbed layers, although not for well-controlled flow fields; they stated that elongational stresses may exert a strong influence on chain dynamics inside adsorbed layers.

As a result of this array of apparently contradictory data and ideas, we initiated a study of the adsorption and desorption of flexible linear polymers subjected to shear and elongational flows near a flat, adsorbing surface. We report here on polystyrene (PS) adsorption and desorption at and around the Θ temperature in two different solvents undergoing flow. Ellipsometry in the dry state was chosen as the surface-sensitive probe, primarily because the method is capable of both fine spatial resolution and high sensitivity to the level of adsorbed polymer; solvent removal also eliminated ambiguities in data interpretation that can arise when ellipsometric measurements are conducted on solvent-swollen films. The experimental setup was not well suited for kinetic measurements, as each time point necessitated a separate experiment on an individually prepared substrate. However, in the absence of flow, a few time-dependent

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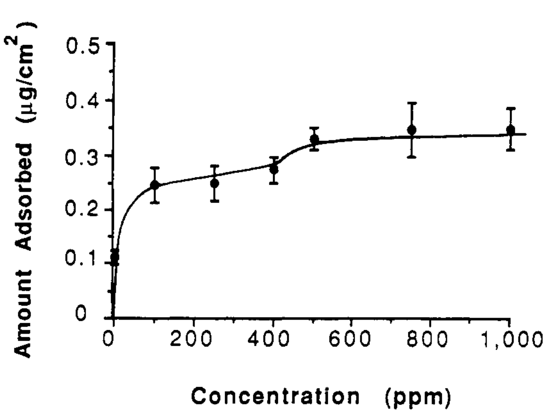

Figure 1. Quiescent steady-state adsorption as a function of polymer concentration for PS ($M_w = 2.95 \times 10^6$) in decalin at 22 °C (adsorption time = 24 h).

measurements were conducted to establish approximate time scales for adsorption. Adsorption kinetics in similar polymer/solvent/surface systems were studied extensively by Lee and Fuller.[1,5]

II. Experimental Section

A. Materials. A single narrow molecular weight distribution PS standard (Polymer Laboratories), $M_w = 2.95 \times 10^6$, was used in all elongational flow experiments. Five molecular weight PS standards were employed in shear flow experiments: $M_w = 4.5 \times 10^5$, 2.95×10^6, and 8.5×10^6 (Polymer Laboratories), 5.5×10^6 (Toyo Soda), and 20.1×10^6 (Polysciences). Solvents were HPLC-grade cyclohexane (Aldrich) or a mixture of 35% cis and 65% trans isomers of decalin (Fisher). Cyclohexane solutions were prepared by slowly suspending the polymer with gentle stirring in heated solvent at 45 °C. These solutions were then stored in an oven at 40 °C; complete dissolution required at least 3 days. Decalin solutions were prepared and stored at room temperature; the Θ temperature of PS in the selected isomer mixture was approximately 18 °C,[15,16] and adsorption experiments were conducted at 22 °C. As with cyclohexane, a lengthy dissolution period was necessary to obtain a homogeneous dilute solution.

PS was adsorbed onto a commercially available (Doran Enterprises) mirror-smooth chrome ferrotype plate, purchased as chromium-coated steel sheets of 1-mm thickness. Substrates cut from these sheets were cleaned according to a literature procedure;[17] in sequence, substrates were immersed in warm toluene for 15 min, dipped in chromic acid for 1 min, rinsed with distilled water, and passed through a flame. At the end of this treatment, ESCA analysis of the top 10-Å surface layer revealed oxidized chromium with a large amount of adventitious carbon (typical atomic composition: 8% Cr, 41% O, 51% C, trace Fe). No further efforts were undertaken to remove carbon-containing impurities, as the goal here was reproducibility in adsorption measurements; multiple measurements were frequently conducted in order to monitor this reproducibility.

Solutions were prepared at sufficiently large polymer concentration to obtain a saturated adsorbed layer at steady state:[18] $C = 1000$ ppm, except for $M_w = 20.1 \times 10^6$ for which $C = 700$ ppm. Figure 1 displays the steady-state adsorption isotherm of the $M_w = 2.95 \times 10^6$ PS standard in decalin at 22 °C. The isotherm is basically of the high-affinity type, with a barely detectable indication of additional adsorption above the initial heel of the isotherm at about 100 ppm. When we used the reciprocal of the intrinsic viscosity as an estimate of the overlap concentration C^*, polymer concentrations were always kept below $0.3C^*$. The time dependence of adsorption for the same sample at 1000 ppm is shown in Figure 2. The adsorption level attained steady state in less than 3 h. Consequently, a standard 5-h adsorption time was established; this period was presumed sufficient to reach steady-state, but not equilibrium, adsorption whenever a polymer solution was exposed to a bare surface. "Steady state" and "equilibrium" in this context denote the time invariant state under flow conditions and under quiescent conditions, respectively. Corresponding concentration- and time-dependent adsorption data for polystyrene in cyclohexane at Θ conditions were reported by Lee and Fuller.[5]

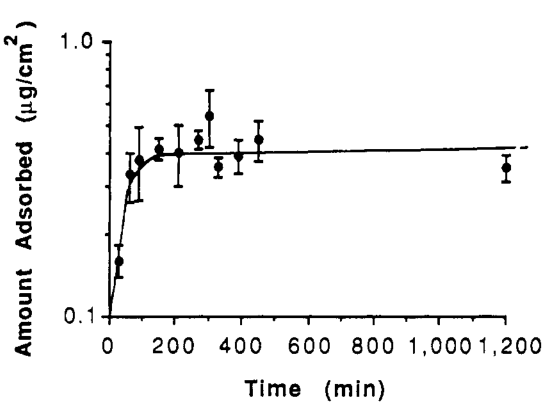

Figure 2. Quiescent adsorption as a function of time for PS ($M_w = 2.95 \times 10^6$) in decalin at 22 °C (concentration = 1000 ppm).

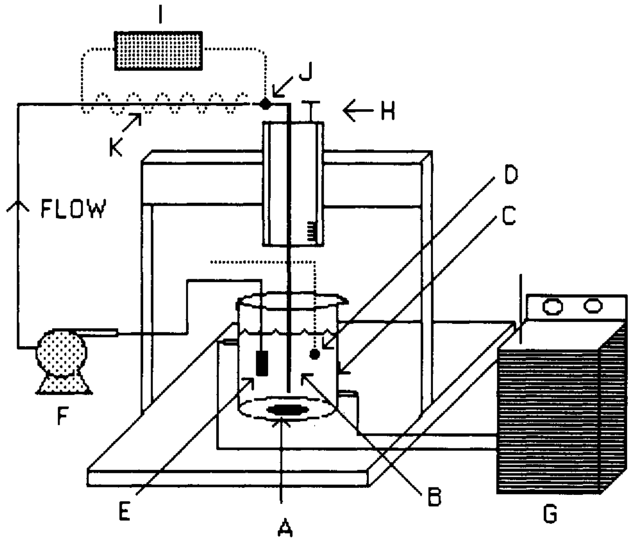

Figure 3. Schematic diagram of the elongational flow device. The parts are labeled as follows: (A) substrate, (B) jet, (C) jacketed beaker, (D) thermocouple, (E) frit, (F) peristaltic pump, (G) water bath, (H) micrometer, (I) temperature controller, (J) needle thermocouple, (K) heating tape.

B. Elongational Flow Device. The elongational flow apparatus is sketched in Figure 3. Along with temperature controls, the key component was a stainless steel jet positioned perpendicularly to the substrate surface. Substrates were first placed horizontally at the bottom of the jacketed beaker and the jet was lowered with a translation stage. With the pump turned on, fluid exiting the jet created biaxial elongational flow near the stagnation point on the surface. The range of nozzle–surface separations corresponding to stable flow depends on both the jet diameter and the nozzle–surface separation;[19] jets of different diameter (0.02–0.2 cm) were interchanged, as needed, to maintain flow stability. The polymer solution was recirculated by a peristaltic pump (Cole-Parmer) through solvent-resistant Viton tubing (Cole-Parmer) extracted of soluble material by preexperiment immersion in heated solvent for 24 h. The inlet to the flow loop was a 2.0-μm stainless steel frit (Anspec) located in the solvent reservoir; the frit eliminated occasional plugging of the jet by particulates. The outer jacket of the double-walled beaker was connected to a ±0.1 °C recirculating water bath (Fisher) for primary temperature control. Additional control was achieved by wrapping the length of Viton tubing leading to the jet with heating tape; a needle thermocouple was inserted at the end of this section, and its temperature was controlled, through the heating tape, by a proportional temperature controller (Digi-Sense by Cole-Parmer). Temperatures at several other points in the system were monitored with thermocouples; the entire scheme permitted regulation of the temperature, and its uniformity throughout the flow loop, to better than ±0.25 °C.

Either of two operating modes could be selected: adsorption from flowing solution or desorption of preadsorbed layers into flowing solvent. In the adsorption mode substrates were initially cleaned, analyzed ellipsometrically, and placed in the jacketted beaker. The jet was then fixed at a surface–orifice separation of 2 jet diameters. Finally, polymer solution was added to the beaker and recirculated at a predetermined flow rate for 5 h. In the desorption mode a steady-state adsorbed layer was first formed by direct exposure of the substrate to a quiescent solution for 12 h. The substrate was then quickly transferred to the jacketted beaker (without drying), where pure solvent impinged on the surface for 5 h.

When either flow protocol—adsorption or desorption—was complete, substrates were removed from the beaker, rinsed immediately with about 50 mL of the appropriate pure solvent at room temperature, air dried, and analyzed by a nulling ellipsometer (AutoEI II by Rudolph Research). A 2.5 × 2.5 cm area around the stagnation point was scanned for layer thickness and refractive index at intervals of 0.25 cm, with somewhat more dense sampling near the center. The operating wavelength was 632.8 nm, and measurements were taken at a fixed angle of incidence (70°). The ellipsometer computed Δ and Ψ, and these quantities were converted to thickness and refractive index by solving the algebraic equations of Drude[17] with a FORTRAN program.[20] In all cases the refractive index of the dried film corresponded to that of bulk PS ($n = 1.59$), and it was assumed that this film also had the density of bulk polystyrene ($\rho = 1.05$). The film thickness could thus be converted to the mass/area of adsorbed polymer. Since the nominal beam diameter of the ellipsometer was not much different from the diameter of the elongational flow dominated surface region, about 1 mm, ability to probe sharp adsorption gradients near the center was limited; sharp gradients were never observed, however, no matter how dense the sampling in the critical region. Only if the elongational flow dominated region was much smaller than 1 mm could it escape detection.

One might intuitively expect that under some conditions the solvent rinse might desorb a fraction of the bound polymer chains. Inasmuch as the rinse step was extremely brief ($\sim$5 s) and only high molecular weight polymers were studied ($M_w > 5 \times 10^5$), desorption here was deemed insignificant. Much longer exposure to the solvent, on the order of hours, would be required to remove significant amounts of PS; desorption measurements provided clear support for this contention. The entire measurement scheme was validated by comparisons to results of previous adsorption investigations,[18,21] principally in the molecular weight dependence of the adsorbed amount; in each case, the agreement was satisfactory.

C. Shear Flow Device. A plane Poiseuille flow device capable of a broad range of wall shear rates (1–1200 s^{-1}) was specially constructed for adsorption/desorption studies. Solutions or solvents were pumped through the shear device by a low pulsation peristaltic pump (Haake-Buchler). Figure 4 shows details of the flow cell. The cell body was created by sandwiching together several machined sections to form a thin slit. On top was a Teflon block, which had been bored to create inlet and outlet channels. The top ends of these channels were connected to the peristaltic pump by Teflon fittings and Viton tubing. The bottom of the cell was a rectangular aluminum block on which the substrate was supported. The flow domain was created by sealing the top and bottom units together against either a Teflon or Viton spacer sheet (Small Parts). The spacer sheets were cut in the middle (see Figure 4) to provide an opening that defined the lateral extent of the shear flow region. Selection of different spacer thicknesses and cutout widths permitted a range of shear rates at a single pump speed.

Experimental protocols in shear flow were similar to those for elongational flow: adsorption from flowing solution or desorption of preadsorbed layers into flowing solvent. With steady shear flow over a flat substrate, however, the adsorbed layer was expected to be nearly uniform across the substrate surface; hydrodynamic calculations showed that the entrance and exit flow disturbances perturbed the parabolic velocity field over only a small fraction of the slit area.[22] Layer uniformity was confirmed by ellipsometry; this extra precaution was necessary, as a steady polymer conformation may not become fully established until some distance from the slit entrance, perhaps at greater distances than those required for achieving steady shear flow. Finally, upon recognition of the diluteness of the test solutions, the velocity fields in both the shear and elongational flow devices were those of Newtonian liquids possessing a viscosity close to the pure solvent's.

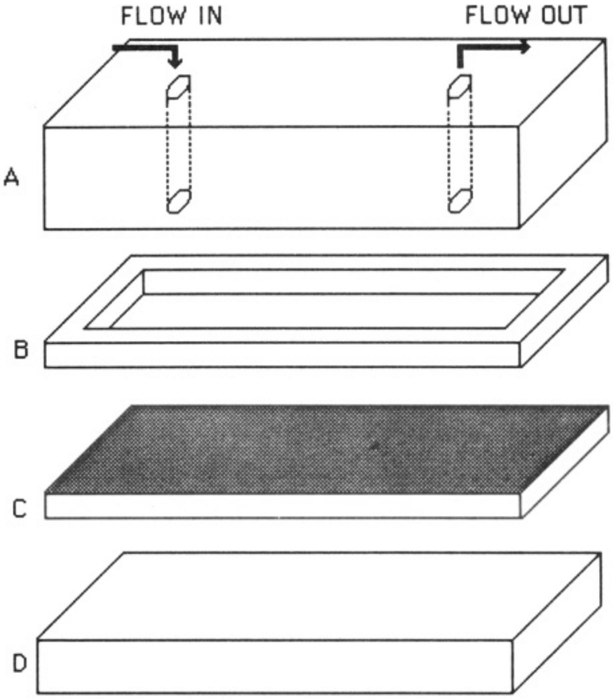

Figure 4. Schematic diagram of the shear flow device. The parts are labeled as follows: (A) Teflon block, (B) cutout sheet, (C) substrate, (D) aluminum block.

It was important to resolve how much chain scission could result from repeated cycling of the polymer solution through the flow loops for either flow device. The $M_w = 20.1 \times 10^6$ PS sample (molecular weight provided by the supplier) suffered some degradation at the largest shear rates studied, at least with decalin as solvent. Prior to the flow experiment we measured $M_w = 21 \times 10^6$ using a low-angle laser light scattering apparatus; after flow we measured $M_w = (12\text{–}13) \times 10^6$. An identical test with the $M_w = 2.95 \times 10^6$ sample in the same solvent revealed no flow-induced degradation. Given the relative insensitivity of the adsorption level to molecular weight, and the similarity in adsorption responses at different molecular weights (see next section), these low degradation levels likely played no role in either decalin or cyclohexane adsorption experiments.

III. Results

A. Quiescent Conditions. Figure 5a shows the amount of PS adsorbed (μg/cm^2) from cyclohexane at 35 °C as a function of molecular weight, with no flow imposed. Data for the same system reported by Stromberg et al.[21] are shown for comparison, and the agreement is good. Reasonable, although not totally quantitative, agreement is also obtained with data by Takahashi et al.[18] for adsorption on electrodeposited chromium. As a final check of the experimental method, material in the adsorbed layer was examined by ESCA and found actually to consist of polystyrene. The error bars on the figure, showing ±1 standard deviation, reflect the statistical variation across a given substrate or when duplicate trials were made, the total variation across all substrates. Most often trials on two or three substrates were conducted, with the adsorption level measured at 15–30 points on each.

Figure 5b shows the analogous molecular weight trend when PS is adsorbed from decalin at 22 °C. The adsorbed amount is lower than that in cyclohexane by a factor of about 2, but the general shape of the adsorption level vs

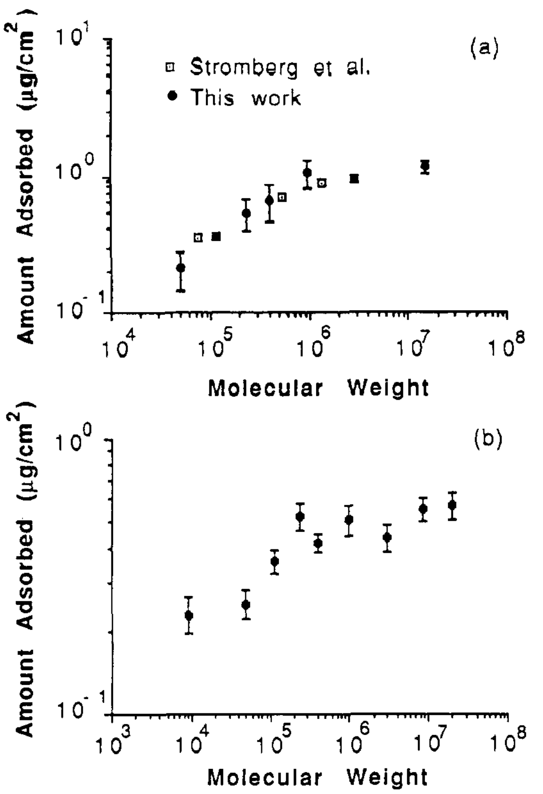

Figure 5. Quiescent adsorption as a function of molecular weight. (a) PS in cyclohexane at 35 °C. (b) PS in decalin at 22 °C (adsorption time = 24 h in both cases).

molecular weight curve is the same. Following the theoretical model of Scheutjens and Fleer[23] for equilibrium polymer adsorption from a Θ solvent, the lower adsorption level in decalin indicates a weaker effective segment/surface interaction (i.e., χ_S, the adsorption energy parameter, is smaller). Assuming temperature-independent segment/surface interactions, χ_S differs solely because of differences in the solvent/surface attraction. Applying Young's equation[24] to the pure solvent above the metal oxide surface

$$\gamma_{SV} - \gamma_{Sl} = \gamma_{lv} \cos \theta_A \tag{1}$$

Here γ_{SV}, γ_{Sl}, and γ_{lV} are energies of the solid–vapor, solid–liquid, and liquid–vapor interfaces, respectively, and θ_A is the contact angle. When the literature surface tension values[25] for decalin (γ_{lV} = 30.7 ergs/cm^2) and cyclohexane (γ_{lV} = 25.2 ergs/cm^2) are combined with contact angles measured on chrome ferrotype plate (decalin, 13.0°; cyclohexane, 16.5°), γ_{Sl} for cyclohexane was found to exceed that of decalin by 5.5 ergs/cm^2. This result supports the explanation suggested for differences in the static adsorption level. Only negligible differences were observed between advancing and receding contact angles.

In both solvents it appears that the adsorption level becomes nearly molecular weight independent for molecular weights above 5 × 10^5; this pattern follows earlier studies,[18] although not the Scheutjens and Fleer theory as applied to Θ solvents. The main message of Figure 5a,b is that this measuring technique can monitor polymer adsorption with acceptable reproducibility and that quiescent adsorption measurements follow expected trends with solvent thermodynamics and molecular weight.

B. Shear Flow. The impact of shear on the adsorption of PS is reported in Figure 6 for decalin and Figure 7 for cyclohexane. In decalin five different molecular weights, all rather large, were studied over a shear rate range from 0 to 1200 s^{-1}; in cyclohexane only two molecular weights were examined, over the same shear rate range. The decalin data are summarized quite simply: for all shear rates studied, flow had no effect on adsorption. In contrast, there was a substantial shear flow effect in cyclohexane, with flow reducing the level of adsorbed polymer. The data of Lee and Fuller[1,5] for PS adsorption from cyclohexane are qualitatively similar to those presented in Figure 7. One feature of their data is slightly different; we found that shear flow caused the adsorption level to decrease continuously with shear rate from the smallest

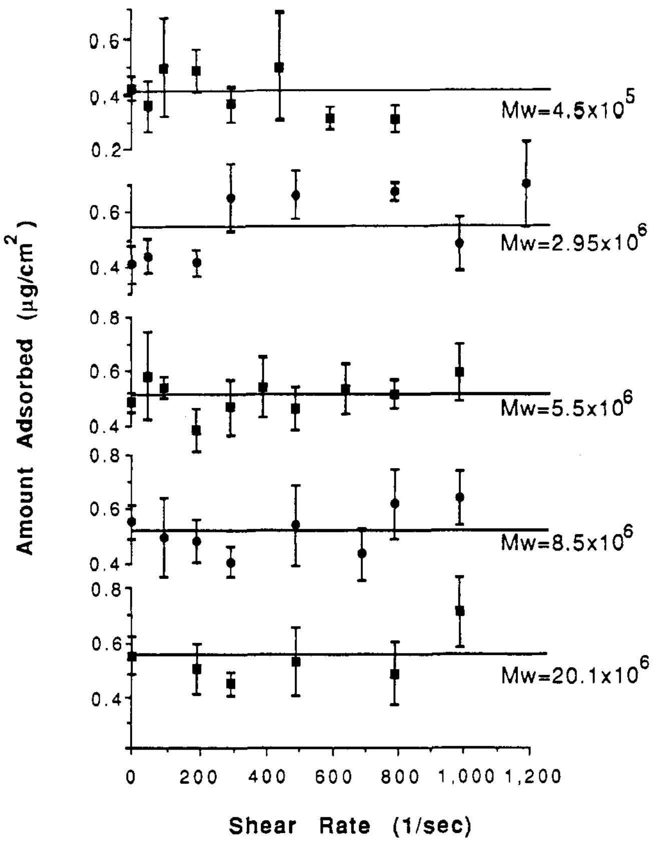

Figure 6. Adsorption of PS from decalin at 22 °C as a function of shear rate. The adsorption time was 5 h, and the polymer concentrations were 1000 ppm, except at M_w = 20.1 × 10^6, for which the concentration was 700 ppm.

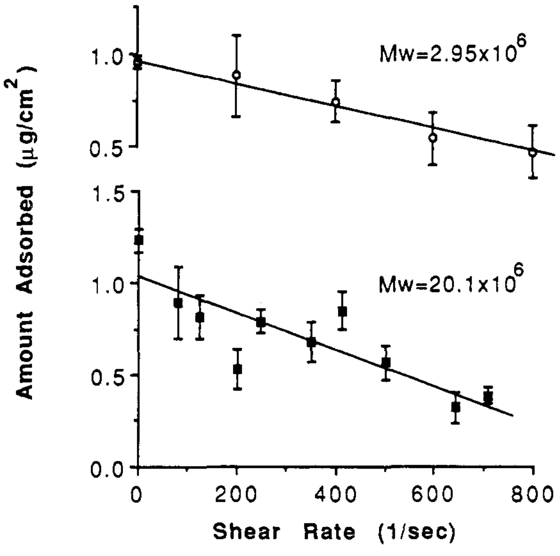

Figure 7. Adsorption of PS from cyclohexane at 35 °C as a function of shear rate. The adsorption time was 5 h, and the polymer concentration was 1000 ppm for M_w = 2.95 × 10^6 and 700 ppm for M_w = 20.1 × 10^6.

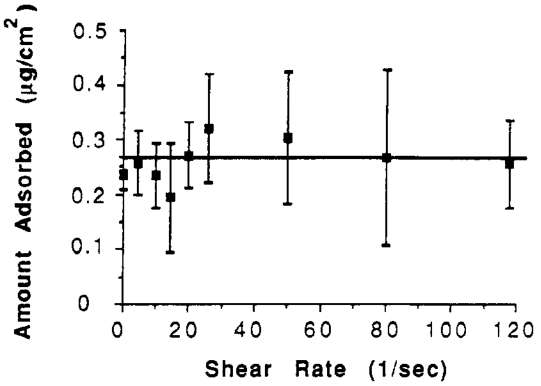

Figure 8. Desorption, expressed in terms of amount retained, of PS (M_w = 2.95 × 10^6) into decalin at 22 °C as a function of shear rate. The desorption time was 5 h.

shear rates examined. Lee and Fuller, however, observed a low shear rate plateau over which the magnitude of the shear rate had no effect on adsorption. For the 20 × 10^6 M_w sample a direct comparison to the earlier study is possible: we found a 35% drop from the quiescent adsorption level at 80 s^{-1} while Lee and Fuller reported essentially no drop until $\dot{\gamma}$ exceeded 500 s^{-1}.

The dimensionless shear rate $\dot{\gamma}\tau$, defined with respect to the single-chain relaxation time τ in bulk solvent, reached a maximum value of about 10 in decalin and 2 in cyclohexane (both maxima were for M_w = 20.1 × 10^6); τ was estimated from $[\eta]\eta_s M_w/RT$, where $[\eta]$ is the intrinsic viscosity and η_s is the solvent viscosity. At any given shear rate, $\dot{\gamma}\tau$ was substantially larger in decalin than in cyclohexane since, at the selected temperatures, decalin has a viscosity approximately 3 times that of cyclohexane (2.48 and 0.755 cP, respectively). Nonetheless, although both are nearly Θ solvents, the effect of flow was greatest in cyclohexane. The lack of a connection between adsorption level and dimensionless shear rate, with solvent quality held nearly constant, indicates that the chain conformation in solution is not regulating the adsorption dynamics at the interface. Consequently, one is led to examine more closely the effect of hydrodynamic forces on previously attached chains.

The desorption of PS into flowing decalin after 5 h was observed to be insensitive to shear rate; this trend is displayed in Figure 8 (in which the abscissa indicates the amount retained after the test period). Lee and Fuller[1,5] found that very high shear rates (2600–7800 s^{-1}) were required to even slightly affect desorption of PS into cyclohexane. It is important to note, however, that Lee and Fuller observed no desorption at low shear rates, while we observed removal of nearly 30% of the adsorbed material at all shear rates studied. Apparently some fraction of the adsorbed layer was bound so loosely that desorption occurred even without the assistance of flow. This reversibly attached fraction probably desorbed, in its entirety, long before the 5-h test period ended, leaving only the tightly bound fraction. Reversibly and irreversibly adsorbed subfractions in an adsorbed PS layer have been reported previously, although not for this surface/solvent combination.[26,27]

It proved impossible to measure the molecular weight of the desorbed chains, given the small adsorbed mass of PS; even with complete desorption of the layer, the polymer concentration in the flow loop would have attained only the level 0.1–1.0 ppm, too low for light scattering or chromatography. Molecular weight information would be helpful in testing whether chain scission or fractionation by molecular weight played a role in the desorption process.

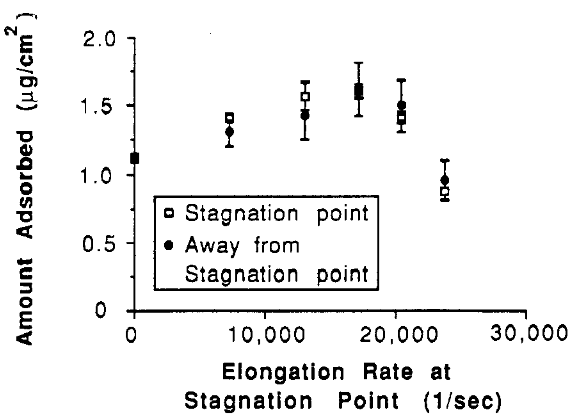

Figure 9. Adsorption of PS (M_w = 2.95 × 10^6) from cyclohexane at 35 °C as a function of the elongation rate at the stagnation point. The two data sets correspond to regions either around or far away from the stagnation point. The adsorption time was 5 h, and the solution concentration was 1000 ppm.

The low polymer concentration in the desorbing solvent, however, justified the assumption that readsorption of desorbed chains was a negligible factor in these experiments. The total volume of the flow loop was about 200 cm^3; solvent or solution cycled through the loop about 10 times, on average, over the course of an experiment. The actual number of cycles depended on the shear rate and slit dimensions. Similar parameters characterized the recirculation of fluid in the elongational flow device.

C. Elongational Flow. Operating in the adsorption mode with the impinging jet, a convected polymer chain suffers a highly unsteady stretching history (unless it becomes trapped exactly at the stagnation point). Figure 9 reveals a decrease, at the highest strain rates, for the adsorption level in regions both close to and far from the impingement point. It is well-known[19] that the flow field close to the stagnation point is nearly pure biaxial elongation (at radial distances less than the jet radius), whereas far away the flow at the surface is simple shear. At distances of the order 1 jet radius, the flow is a combination of shear and elongation, and the shear rate at the surface attains its maximum value. Results for positions distant from the impingement point are consistent with the simple shear results presented earlier; a characteristic shear rate for the distant region was of the order 500–2000 s^{-1}. The adsorption level at the stagnation point also decreased at the highest elongation rate. Relative to adsorption under quiescent conditions, however, the decreases were not large at any position (27% at the stagnation point and 17% far away). At lower strain rates it appeared that the adsorption level increased with strain rate, but this trend is barely discernable above the uncertainty in the data.

Findings for the desorption of PS from elongational flow are shown in Figure 10. The amount retained from a quiescently adsorbed layer, after exposure to flowing cyclohexane for 5 h, is plotted as a function of elongation rate. Although the error bars are large, it appears that the flow field had no effect on desorption. As in the earlier shear flow experiment, a large fraction of the layer has desorbed in this time frame, with or without flow. Some investigators have reported essentially irreversible adsorption for the same system;[1,28] the discrepancy could well arise from variations in surface chemistry or surface roughness produced by different surface preparation procedures.

No "bulls-eye" patterns were seen when carrying out either adsorption or desorption experiments from elon-

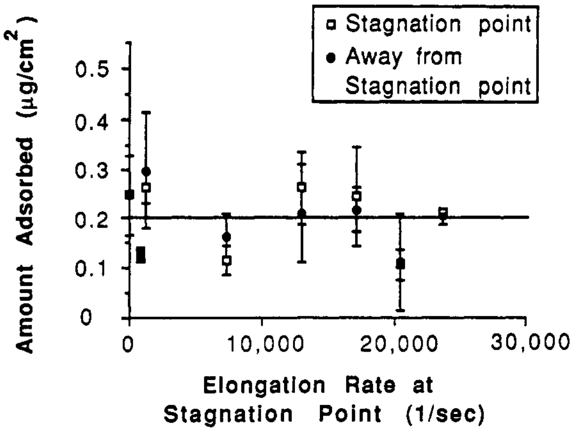

Figure 10. Desorption of PS ($M_w = 2.95 \times 10^6$) into cyclohexane at 35 °C as a function of the elongation rate at the stagnation point. The two data sets correspond to regions either around or far away from the stagnation point. The desorption time was 5 h.

gational flow. We believe that the curious rings observed previously by Besio et al.[3] arose from dissolved or suspended impurities. These impurities could also account for the adsorption increase with time observed by these authors during desorption experiments. We introduced a low concentration impurity (silicone grease) in our system to test this suspicion. When a desorption experiment was performed, rings of the type described by Besio et al. were clearly visible; we could not identify the chemical identity of the material actually composing the rings. Our belief is that the rings were created by alterations/instabilities in the base flow at large radial distances.

IV. Discussion

A detailed explanation of the influence of flow on polymer adsorption is clearly not yet possible, and most discussions based on the present data can only be regarded as speculations. Nonetheless, some general ideas are suggested. Given the similarity in responses for shear and elongation, it appears that the polymer conformation in the bulk fluid above the surface is irrelevant. This finding is buttressed by the lack of a correlation between known changes in the bulk chain conformation and the adsorption level. In the elongational adsorption results of Figure 9, for example, the *De* for the flow at the stagnation point varied from 0 to 2.3, a range over which it is known that the polymer conformation in the bulk solvent changes drastically. Nevertheless, the elongation-affected surface region yielded the same adsorption level as regions where the polymer conformation was unaffected by flow. A final argument for this conformation independence is that the two Θ solvents provided shear flow adsorption results inverted from the ordering expected from their viscosities.

For the entire strain rate ranges studied, neither flow type had a significant impact on the desorption of preadsorbed layers. At the same time, however, appreciable desorption did occur for both solvents. Curiously, in both decalin and cyclohexane the amount of polymer remaining on the chromium surface after 5 h of desorption was nearly the same, ~0.2–0.3 μg/cm². These results taken together suggest that two polymer subpopulations existed at the surface, one tightly (irreversibly) bound and the other loosely (reversibly) bound. Further evidence of a dual population can be extracted from the adsorption isotherm in decalin, which showed an initial plateau at the same adsorption level as that monitored after desorption of a more highly adsorbed layer. This coincidence suggests that an initial fraction of chains was held tightly to the surface and that these chains were unaffected by flow. A second, more loosely attached fraction of chains then adsorbed (under quiescent conditions), chains that could subsequently desorb into pure solvent so readily that complete removal occurred in 5 h, with or without flow. In the adsorption mode, on the other hand, the attachment of these weakly bound chains was modified by flow, which perturbed the competition between solvent molecules and chain segments for the available surface sites; this perturbation then altered the total surface density of chains. If this speculative interpretation is correct, the adsorbed layer was always far from equilibrium.

The number of loosely held chains was presumably larger in cyclohexane than in decalin, inasmuch as the quiescent adsorption level was higher. If these chains constituted the flow-affected population, this difference explains why flow had its greatest effect in cyclohexane. In fact, given the experimental uncertainty in the adsorption measurements with flow, changes in the number of loosely bound chains in decalin probably would not be noticed since their adsorption level was so low; this explanation is consistent with the lack of a significant flow effect for decalin during adsorption on a bare surface (see Figure 6).

Why two subpopulations should exist in an adsorbed layer is not understood, although similar conclusions have been reported for a variety of polymer/solvent/surface combinations.[26,27,29,30] Certainly, such subpopulations must be fuzzy. In our case, the inability to reach equilibrium could well be related to the extremely high molecular weights employed. An additional factor in formation of a nonuniform adsorbed layer could be surface inhomogeneity, remembering that ESCA analysis revealed a complex chemical composition for the surface of the ostensibly clean chrome ferrotype plate. Further understanding of the development of adsorbed layer structure in flow will obviously necessitate more detailed studies of adsorption and desorption kinetics under various flow histories; employing Θ solvents for this purpose will remain desirable since their selection simplifies the description of the solvent/segment thermodynamic interaction, as well as permitting the solvent/segment hydrodynamic interaction to be unified by the viscosity.

It is noted that one of the systems discussed, high molecular weight PS in decalin, was reported by the Bristol group to form an adsorption-entanglement layer under steady shear flow.[10,32] With the experimental protocols employed here, we suspect a thick adsorption-entanglement layer would be readily apparent; in fact, we have seen no evidence of the adsorption-entanglement phenomenon. Several theories for polymer adsorption and polymer layer properties under flow have been formulated,[5,33-35] but the number of assumptions is always large and actual applications to the present data would appear premature. The major difficulty is the proper treatment of chain/chain interactions and hydrodynamics inside a dense, solvent-swollen polymer layer. None of the present theories postulates a dual chain population containing reversibly and irreversibly bound fractions.

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