

# Segmental orientations of trains versus loops and tails: the adsorbed polymethylmethacrylate system when the surface coverage is incomplete

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## Abstract

We measure, for the first time, the separate surface coverage-dependent orientations of trains and of loops/tails in the structure of an adsorbed polymer, and show that these have different average orientations. The system was PMMA (atactic polymethylmethacrylate) adsorbed onto oxidized silicon from dilute solution in carbon tetrachloride at 25.0°C. The method was FTIR-ATR (infrared spectroscopy in attenuated total reflection). With increasing surface coverage, train segments were observed to maintain constant average anisotropy with respect to the solid surface. Free segments were preferentially flattened when the surface coverage was low, but with increasing surface coverage became progressively more random in orientation. Free and bound segments were separated according to shifts of the vibrational frequencies of carbonyl segments upon hydrogen-bonding to the surface silanol groups. The dependence of segmental orientation on molecular weight of the chain is also discussed. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The usual theoretical analysis of polymer adsorption is coarse-grained; chains are modelled as trajectories on a lattice [1] or as mathematical curves [2] and one does not seek to explain molecular details of the orientation of polymer segments in their adsorbed states.

The purpose of this short paper is to inquire experimentally into a property at a more chemical level — the mean segmental orientation. Given the importance of polymer adsorption phenomena — in applications that range from cosmetics and magnetic recording coatings, to paints, food, medicines, and lubrication — it is worthwhile to inquire into these chemical problems. The main original contribution of this study is to provide new experimental data concerning segmental orientation, especially the distinction between seg-

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mental orientation in trains and loops/tails, at variable surface coverage.

The proposition that conformations of adsorbed flexible polymers have a history-dependent conformational distribution has been advanced by experimentalists for many years. Evidence in favor was first advanced during the 1960s and 1970s by Grant, Smith, Stromberg, and Passaglia [3,4]. During the 1980s, Pefferkorn, Haoum, and Varoqui proposed the ‘hairy carpet’ model [5–7] which recognized that chains first arriving at a surface adsorb in relatively flat conformations, while those arriving later become adsorbed in more loosely bound configurations. Even more recently, a similar view comes independently from Monte Carlo simulations of Zajac and Chakrabarti [8]. Nonetheless there is a countervailing point of view which presumes that the conformations of adsorbed polymers are equilibrated [1]. The present laboratory has also worked experimentally on this problem [9–13]. We have proposed unifying principles to characterize distribution of conformations within non-equilibrium adsorbed polymer layers and find that the conformational distribution is dominated by the surface coverage at the point of impact with the surface [14]. We have proposed that this ‘parking problem,’ adsorption of a large reservoir of adsorbate onto an initially-bare surface of limited area, presents analogies with many other physical systems in the everyday world — from economics to biology [14].

In this paper dealing with adsorbed polymers, we focus upon the orientation of individual adsorbed segments within an adsorbed layer with special attention upon the circumstance of incomplete — ‘starved’ — surface coverage. We have in mind the idea that issues of segmental orientation may play a particularly significant role in situations where functional groups are introduced into polymer chains to impart desired electrical or optical properties, or to modify adhesion forces or dispersion qualities. Here we present preliminary results, in a model system, which demonstrate substantial difference between those segments that were in physical (hydrogen-bonded) contact with the surface and those that were not.

## 2. Experimental

The liquid cell used for these measurements employed Fourier transform infrared spectroscopy in attenuated total reflection, FTIR-ATR, as has been described elsewhere [9–11]. The ATR crystal was a trapezoidal silicon element ( $52 \times 20 \times 2$  mm in dimension) with the incidence angle of  $45^\circ$ . A KRS-5 wire grid was used to manually select the IR polarization and a mercury-cadmium-telluride (MCT) detector was used to detect the absorption with a Bio-Rad FTS60A FTIR.

The mass adsorbed was quantified by methods described previously [9]. In brief, calibrations were made within the ATR cell of the absorbance from a solution of known bulk concentration when it was exposed to the silicon crystal after it had been treated by coverage with a self-assembled methyl-terminated organic monolayer to be non-adsorbing. The calibration of surface coverage (mass per area) was based [9] on knowing the penetration depth of the evanescent wave. These calibrations also were the basis of subtracting, from a given ATR signal, the calibrated contribution of polymer that was free in the bulk solution of known concentration [9].

To quantify orientation within the adsorbed layers, an analysis presented previously based on the Flournoy–Shaffers relations [15] was employed [16]. Briefly, measurements of infrared absorbance in the *p* direction (parallel to the incident plane) and *s* direction (perpendicular to the incident plane) were analyzed to deduce the infrared absorbance in the Cartesian direction parallel to the solid surface ( $A_x \equiv A_y$ ) and perpendicular to the solid surface ( $A_z$ ). The dichroic ratio was defined as the ratio of absorbance in these two orthogonal directions:

$$D \equiv A_z/A_x \equiv A_z/A_y \quad (1)$$

Thus  $D = 1$  for an isotropic sample and  $D < 1$  if the dipole moment of an infrared oscillator is preferentially oriented parallel to the surface.

The samples of atactic polymethylmethacrylate (PMMA) were purchased from Polymer Laboratories. Properties of these samples are listed in Table 1. The carbon tetrachloride solvent was

purchased from Aldrich and used as received. Methods to calibrate the infrared signals and to oxidize the silicon to produce a reproducible, controlled oxide layer were described previously [11]. The temperature was controlled at 25.0°C. The quantity of PMMA adsorbed was controlled by temporarily introducing dilute PMMA solution ( $\approx 0.05 \text{ mg ml}^{-1}$ ) into the liquid cell for several seconds, then replacing the solution by pure solvent. After equilibration for 1 h, sample spectra were collected in p and s polarization. These procedures were continued sequentially under the surface coverage had saturated. Control experiments showed that changing the amount adsorbed in each sequential step did not change the results. The mass adsorbed at saturated surface coverage was measured with the surface exposed to a polymer solution of higher concentration,  $\approx 1 \text{ mg ml}^{-1}$ .

### 3. Results

From the known shift to lower wavenumber when a carbonyl group experiences hydrogen bonding [17,18] (in the present physical situation, this is hydrogen bonding to silanol groups on the surface of the oxidized silicon) the ‘bound’ and ‘free’ mass adsorbed were determined after integrating the absorbance peaks using curve-fitting methods similar to those described elsewhere [11]. The shift was from a band centered at  $1732 \text{ cm}^{-1}$  to a band centered at  $1710 \text{ cm}^{-1}$  and, using curve-fitting methods, these could be nicely separated [11,13]. The absorptivity of these peaks may differ in principle [18]. Past publications from this laboratory have endeavored to take the expected

difference in absorptivity into account when calculating the mass adsorbed [11,13]. Here, in view of the arbitrary nature of those assumptions, the bound fraction was defined simply as the ratio of bound mass to total mass adsorbed.

Relative changes are meaningful despite this uncertainty regarding the relative absorptivity of these two vibrational bands. Another uncertainty is the absolute magnitude of  $D$  owing to residual surface roughness on the polished silicon crystals, but again relative changes are meaningful with respect to this quantity. In addition, since the dipole moment of the carbonyl stretch is parallel to the C=O bond, the observed  $D > 1$  (see discussion below) implies that C=O bonds tended to be oriented vertical to the surface. Consideration also shows that the direction of C=O bonds is preferentially perpendicular to the polymer backbone [11].

Table 1 summarizes the saturated bound mass adsorbed and the total mass adsorbed for polymers whose molecular weight spanned two orders of magnitude, from  $10^4$  to  $10^6 \text{ g mol}^{-1}$ . The total mass adsorbed increased somewhat with increasing molecular weight, as anticipated from general principles [1,2], however, the bound mass was almost constant. Therefore the bound fraction decreased with increasing molecular weight. The number of PMMA segments in hydrogen-bonded contact with the silicon oxide surface was determined by local properties of the polymer segments and the surface — not by the chain’s molecular weight.

The situation was different when the surfaces were ‘starved,’ i.e. when surface coverage was incomplete. In Fig. 1, the bound fraction of adsorbed PMMA with different molecular weight is plotted against the mass adsorbed. In lower coverage case the bound mass was less, the higher the molecular weight of the adsorbing polymer. This implies that the structure of these polymers was less localized in trains on the surface. This was also reflected in the dichroic ratio.

In Fig. 2, the dichroic ratio of the carbonyl stretch of bound segments is plotted against the mass adsorbed. There was no systematic change with surface coverage: within the experimental scatter,  $D = 1.0 - 1.1$  regardless of surface cover-

Table 1  
Polymer molecular weights and quantities adsorbed

$M_w \text{ (g mol}^{-1}\text{)}$	$M_w/M_n$	$\Gamma_{\text{bound}} \text{ (mg m}^{-2}\text{)}$	$\Gamma_{\text{total}} \text{ (mg m}^{-2}\text{)}$
$2.7 \times 10^4$	1.11	0.37	1.75
$7.4 \times 10^4$	1.07	0.36	1.81
$2.2 \times 10^5$	1.05	0.36	1.94
$8.2 \times 10^5$	1.04	0.37	2.02
$2.2 \times 10^6$	1.08	0.36	2.16

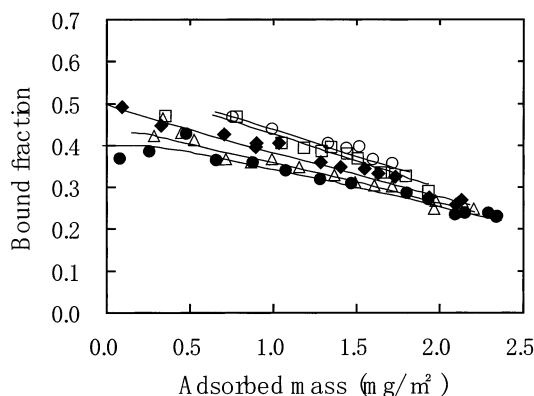


Fig. 1. The bound fraction of PMMA (atactic polymethylmethacrylate) adsorbed onto oxidized silicon from dilute carbon tetrachloride solutions is plotted against the total amount adsorbed. The bound fraction was determined from 'bound' and 'free' carbonyl vibrations in the infrared spectra, assuming that the absorptivity of 'bound' peak was 50% enhanced. Typical error size is about 20% for lower adsorbed mass region, 10% for higher region. The molecular weight of the atactic PMMA chains was varied:  $M_w = 2.2 \times 10^6$  (filled circles);  $M_w = 8.2 \times 10^5$  (up-triangles);  $M_w = 2.2 \times 10^5$  (filled diamonds);  $M_w = 7.4 \times 10^4$  (open circles) and  $2.7 \times 10^4$  g mol<sup>-1</sup> (open squares).

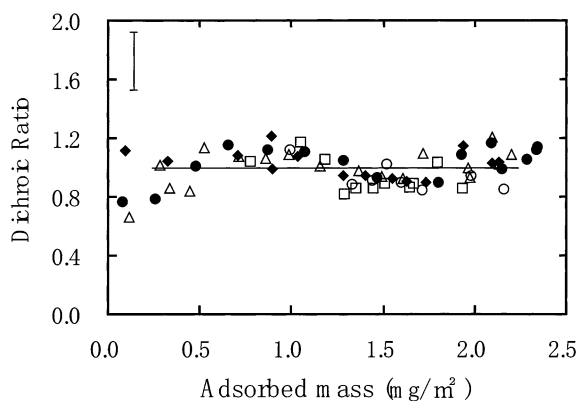


Fig. 2. The dichroic ratio of the bound carbonyl vibrations, determined from the ratio of infrared absorption in p and s polarization, is plotted against the total amount of PMMA adsorbed. Typical error scale is shown on the left-upper corner of the figure. Symbols have the same meaning as in Fig. 1.

age, indicating that orientation is isotropic on the average, or nearly so.

But the situation was quite different for the free carbonyl segments. In Fig. 3, the dichroic ratio of the carbonyl stretch of free segments is plotted

against mass adsorbed. Here the trend was that  $D > 1$  except for saturated layers, indicating that the conformation of tails and loops was relatively more flattened under these conditions of incomplete surface coverage. Particularly interesting is the dependence on molecular weight: chains of lower molecular weight showed higher dichroic ratio than chains of higher molecular weight, indicating that the former were relatively more flattened.

#### 4. Future prospects

In this study we have shown distinct differences between the segmental orientation of trains and loop-tail structures within an adsorbed polymer layer. Within the train structure, the mean segmental orientation was 'frozen' at the value taken when the chains first adsorbed, and did not change with additional time elapsed or additional amount adsorbed. Furthermore, when the surface coverage was less than complete, loops and tails within the shorter PMMA chains were more flattened than for the longer chains. Therefore the thickness of the adsorbed layer must be higher for the longer chains.

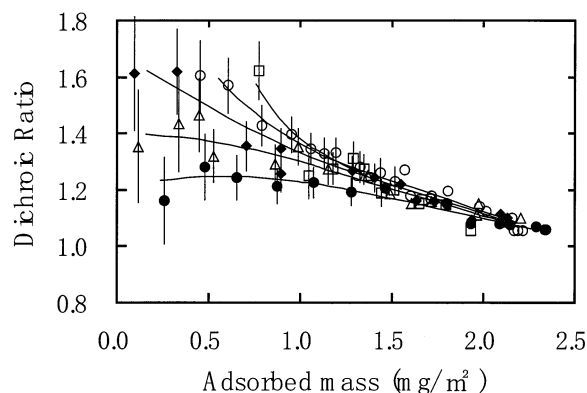


Fig. 3. The dichroic ratio of the free carbonyl vibrations, determined from the ratio of infrared absorption in p and s polarization, is plotted against the total quantity of PMMA adsorbed. Typical error size is about 15–20% for lower adsorbed mass region, <10% for higher region. Symbols have the same meaning as in Fig. 1.

The adsorption process involved the well-known transition, from a chain's random coil configuration in free solution, to a chain's flattened configuration on the surface [3–14]. The final state may be influenced by the extent of equilibration that can be accomplished before adsorption of many segments traps the chain in a frozen adsorbed state. This study has presented a quantitative evaluation of how far this equilibration proceeds.

We conclude with the interesting technological possibility that these thoughts may provide a strategy to control the surface morphology of dispersed pigments. In an idealized equilibrated state [1], the structure of adsorbed polymers is controlled by materials properties such as molecular weight, adsorption energy, and concentration in the bulk. But if one takes seriously the proposition that that transient states of structure may have a long lifetime, when dealing with adsorbed polymers [3–14], this opens new possibilities. Motivated by the data presented here, we suggest that it should also be possible to control these surface structures by using the time factor of adsorption history, and by modifying the mixing history judiciously.

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