

## Conformational States of Polymers Adsorbed on Interfaces

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**ABSTRACT:** Adsorbed layer thickness ( $t$ ) of several dilute polymeric systems were measured by ellipsometry. For physically adsorbed homopolymers,  $t$  scales as  $M^{0.5}$  and  $M^{0.4}$  in theta and good solvents, respectively. Conformational change from "mushroom" to "brush" were observed for a terminally attached polyelectrolyte by adjusting electrostatic "excluded volume". By applying potential for polyelectrolytes adsorbed on a metal surface, both stretched and squeezed conformations were realized. Stiff polymers can be adsorbed either end on or lying flat configurations. Intercalation adsorption into clay lamellas, i.e. slits resulted disk-like conformation. Thus, the concept of "conformation control of adsorbed polymers" was experimentally realized.

**KEY WORDS** Adsorption / Ellipsometry / Layer Thickness / Conformation / Terminally Attached Chain /

Adsorption of polymers on surfaces and interfaces has key roles in a wide variety of fields, such as adhesion, flocculation, stabilization of colloidal particles, reinforcement in composite and biological processes.<sup>1~4</sup> The features are quite different from those of adsorption of small molecules. Figure 1 depicts various adsorbed conformations for flexible and stiff or rod-like polymers. It should be noted that conformational varieties are more abundant than those in solution.

In the above application fields, it is often necessary to control the adsorbed conformation of polymers to adjust interaction between adsorbed polymer layers. However, before to obtain such control methods, determination of the conformations of adsorbed polymers is one of the most important problems. For determination of conformations, measurements of adsorbed layer thickness and, if possible, segment density distribution normal to the surface are required. In this article, I employed mainly ellipsometry to measure the adsorbed layer thickness and explore conformational control methods experimentally.

### RESULTS

#### A) Physically adsorbed polymers

It is now well established that physically adsorbed polymers are held on the surface by relatively few attached segments and the remaining segments form loops and tails. At the theta point, we showed that ellipsometric layer thicknesses  $t$  of both polystyrene (PS)<sup>5</sup> and sodium poly(styrene sulfonate) (NaPSS)<sup>7</sup> are proportional to the square root of molecular weight. In good solvent condition,  $t$  scales  $M^{0.4}$  for both PS and NaPSS. Note that the coil radius  $R_g$  in solutions scales  $M^{0.6}$ . Ellipsometric thickness is given by

$$t_e = \Gamma^{-1} \int_0^{\infty} C(z) z dz \quad (1)$$

where  $z$  is the distance to the wall (Figure 2),  $\Gamma$  is the adsorbance and  $C(z)$  is the concentration at the distance  $z$ . We presented the argument based on de Gennes scaling theory to show

that the exponent should be 0.4 in good solvent condition.<sup>6~9</sup> That is, the local volume fraction  $\phi(z)$  is given by

$$\phi(z) \sim v_0 C(z) \sim (a/z)^{4/3} \quad (a < z < R) \quad (2)$$

where  $v_0$  is the monomer volume and  $a$  is a monomer size. The cut off  $R$  is comparable to a random coil size  $R \sim aN^{3/5}$ , where  $N$  is the degree of polymerization. Inserting (2) into (1), one finds

$$t_e = \int_0^R \phi(z) z dz \sim aN^{2/5} \quad (3)$$

The exponent 0.4 is also observed for the other polymer-solvent-adsorbent systems as shown in Figure 3, in which surface force apparatus<sup>10</sup> and evanescent wave method<sup>11</sup> were used to measure layer thickness. Thus, we may conclude that the physically adsorbed polymer layers have a self-similar structure.

#### B) Terminally attached chains

Terminally attached chains can be formed by three ways. The first is to prepare polymers whose one end is capped with polar groups. An example is shown in Figure 4(a), in which a very polar

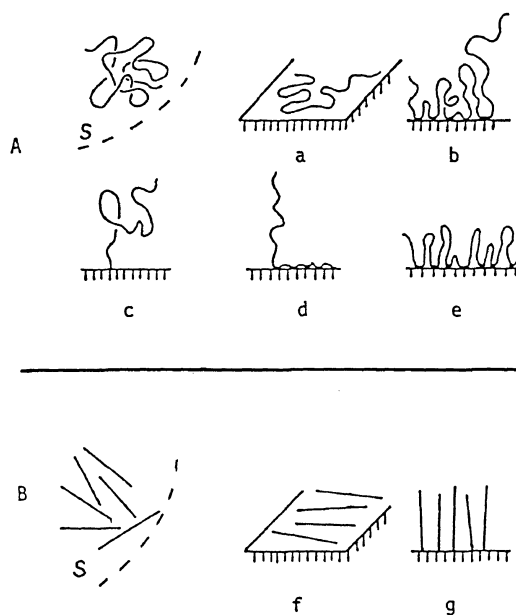


Figure 1. Various conformations of polymers adsorbed at an interface. (A) flexible polymers; (B) rodlike polymers: (S) in solution, (a-g) adsorbed at the interface; (a,f) lying flat; (b) loop-train-tail; (c,g); terminally attached; (d) train-tail; (e) loop-train.

functional group 1,1 bis(p-N,N'-diethyl aminophenyl) methanol is attached to polybutadiene (T-PBR).

The second is the surface grafting and the third method is to employ block copolymers whose one block is preferentially adsorbed on a surface and the other blocks are protruded into solution phase. If the surface density of polymers is low, we have separate "mushrooms", with the coil size  $R_g$ , and if the density is high, we have the "brush" as shown in Figure 2(c) and (d).<sup>12</sup> In the latter case, the overall thickness of the brush is given by

$$L = Na(a/D)^{2/3} \quad (4)$$

where  $D$  is the average distance of chains.<sup>13</sup>

Comparison of the adsorption data of T-PBR with that of a conventional PBR is made in Table I to show the effect of the polar terminal functional group.

The difference in  $A$  and the surface coverage of the silanol groups  $\theta$  at the silica surface is due to the preferential adsorption of the terminal polar group on T-PBR over that of the butadiene units on PBR.<sup>14 ~ 16</sup>

With respect to carbon black reinforcement, Nagata et al<sup>17</sup> have revealed that styrene-butadiene copolymer (T-SBR) terminally functionalized with the same group causes a large reduction in carbon-to-carbon hysteresis and large increases in resilience and in modulus at high extensions. This study also indicates that instead of

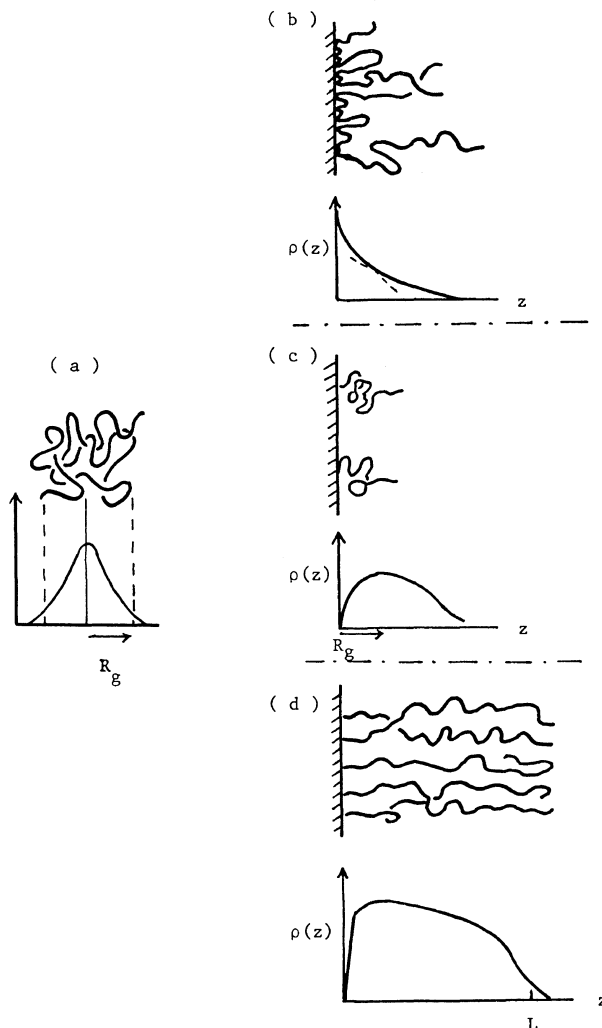
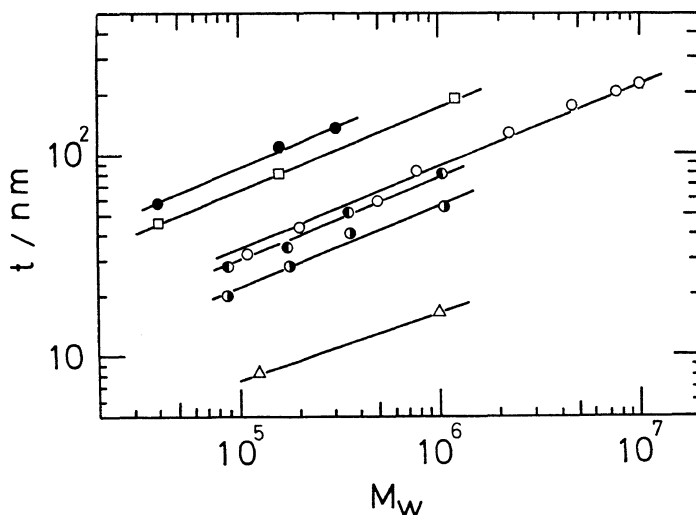


Figure 2. Schematic of the conformations and corresponding segment densities for (a) a random coil in solution, (b) physically adsorbed chain (loop-train-tail); (c,d) terminally attached chains to a wall [(c) mushroom and (d) brush regimes].



**Figure 3.** Double logarithmic plot of  $t$  against  $M$  for several polymer-good solvent-adsorbent systems: polystyrene- $\text{CCl}_4$ -Cr at  $35^\circ\text{C}$ ,  $\circ$  ; poly(ethylene oxide)-toluene-Mica at  $21^\circ\text{C}$ ,  $\bullet$  ; PEO- $0.1\text{MKNO}_3$ -Mica at  $23^\circ\text{C}$ ,  $\square$  ; Na poly(styrene sulfonate)- $0.1\text{M NaCl}$ -Pt at  $25^\circ\text{C}$ ,  $\bullet$  ; NaPSS- $0.5\text{MNaCl}$ -Pt at  $25^\circ\text{C}$ ,  $\bullet$  ; poly(methylmethacrylate)-toluene-sapphire at  $20^\circ\text{C}$ ,  $\triangle$  . Except PMMA, the lines are drawn with a slope of 0.4.

covalent bonds, rather salt formation or hydrogen bonding which are labile under stress is very effective for the reinforcement.

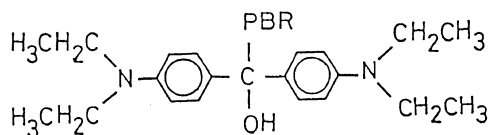
The block copolymer which possesses polyelectrolyte blocks as shown in Figure 4(b), has a marked feature that exhibits conformational transition from "mushroom" to "brush" conformations by adjusting electrostatic "excluded volume" interactions between charged groups on the block chains with ionic strength. Figure 5 shows the result of salt concentration dependence of ellipsometric thickness for the ionene-EO-ionene block copolymer adsorbed at the air-aqueous KBr solution interface.<sup>18</sup> With decreasing KBr concentration, thickness increases from  $R_g \equiv \langle S^2 \rangle^{1/2}$  of the ionene block to the fully stretched (contour) length  $L$ , while the  $R_g$  of ionene polyelectrolyte alone never reaches to  $L$  as shown in Figure 5.

**Table I.** Adsorption data of T-PBR and PBR on silica at the plateau region at  $25^\circ\text{C}$  (CH: Cyclohexane)

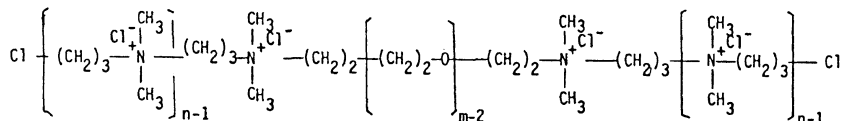
Sample	$M_n/10^3$	$A \cdot 10^8 (\text{gcm}^{-2})$		$\theta$		$p$	
		CH	$\text{CCl}_4$	CH	$\text{CCl}_4$	CH	$\text{CCl}_4$
T-PBR	222	8.5	5.9	0.65	0.26	0.25	0.12
PBR	207	7.3	2.4	0.50	0.15	0.25	0.15

\*)  $p$  is the fraction of adsorbed monomer units per polymer.

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( a )



( b )

**Figure 4.** (a) Terminally functional poly(butadiene).  
(b) 3-3 ionic-ethyleneoxide triblock copolymer.

C) Conformational changes of adsorbed polyelectrolyte by applied potential.

Polyelectrolytes, such as sodium salt of poly(acrylic acid), sodium poly(styrene sulfonate)(NaPSS) and deoxyribonucleic acid are adsorbed on metal surfaces. Adsorption of NaPSS from aqueous NaCl solution onto a platinum plate was studied by ellipsometry.<sup>19,20</sup> At rest potential the ellipsometric thickness scales as  $M^{0.5}$  and  $M^{0.4}$  in theta and good solvents, respectively. By applying potentials, which correspond to cathodic and anodic potential differences relative to the rest potential, we could change adsorbed NaPSS conformation depending on the sign of potentials as shown in Figure 6 and 7. At the negative potential differences, NaPSS stretches markedly, while at the positive potential differences, it is squeezed probably resulting loop-train conformation.

D) Adsorption of stiff and rodlike polymers

In general, for stiff polymers two principal adsorbed configurations are possible as shown in Figure 1(f) and (g). It was shown that both poly- $\gamma$ -benzyl-L-glutamate and polyglutamic acid in their helical form adsorb in the standing on end configuration, since their adsorbed layer thicknesses measured by ellipsometry were almost equal to the length of these rodlike polymers<sup>2</sup>.

(Hydroxypropyl) cellulose (HPC) has many OH groups at the ends of side chains, which interact with surface OH or O groups of a metal. Moreover, HPC is a liquid crystal forming polymer and is fairly stiff, since its persistent length in water is 18.2 nm. The adsorbed layer thickness of HPC on a platinum foil measured by ellipsometry reveals that the layer thickness is almost 2 ~ 5 nm irrespective of molecular weight of HPC. Since the width of HPC is 1 nm, and judging from the value of persistent length, HPC behaves intermediate between rodlike molecule and a random coil, the observed thickness indicates somewhat wormlike adsorbed conformation whose height of loops is as high as 5 nm. Thus, HPC adsorbs fairly flat configuration on Pt from water.<sup>21</sup>

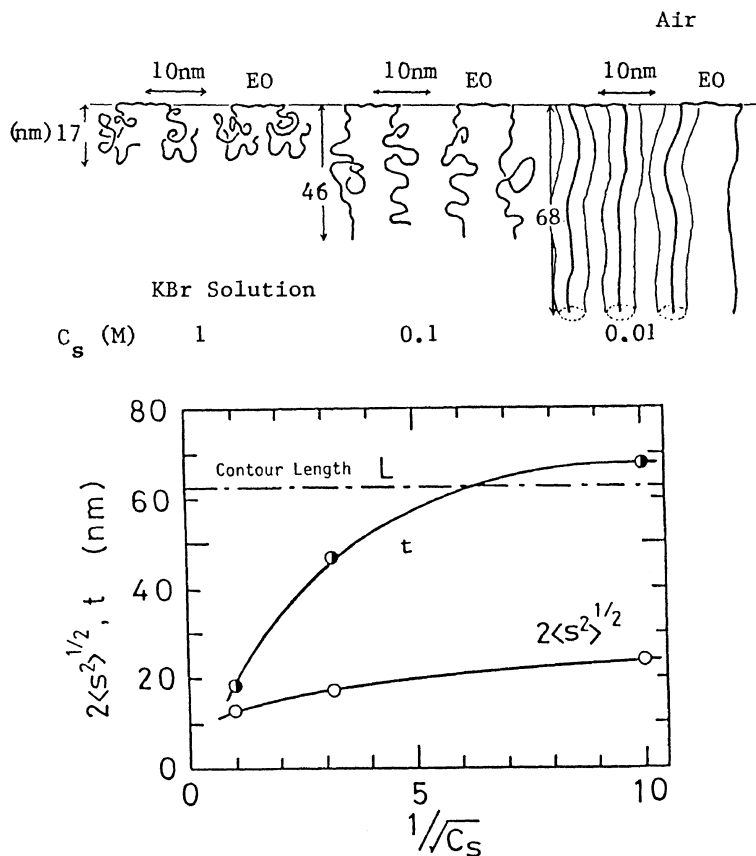


Figure 5. Conformation changes of adsorbed ionene-ethylene oxide block copolymers from "mushroom" regime to "brush" regime.  $t$ , layer thickness and  $\langle s^2 \rangle^{1/2}$ , radius of gyration.

#### E) Adsorption in various geometries

Since the polymer adsorption on a flat surface is rather exceptional in practice, and adsorption on restricted dimensions as well as various geometries<sup>22,23</sup> is important as shown in Figure 8. Studies in these directions have been exploited. Here, as an example, I show the polymer adsorption in the slit<sup>24</sup> which is shown in Figure 8(c).

Adsorption of poly(ethylene oxide)s (PEO) on calcium montmorillonite (specific surface area 788 cm<sup>2</sup>/g) from their aqueous solutions was studied. High molecular weight PEO showed high affinity type adsorption isotherm. Concomitant measurement of  $d(001)$  spacing of the clay by X-ray diffraction indicates that interlayer spacing is 0.7 nm when the degree of polymerization  $N$  exceeds  $10^3$  and is independent of  $N$ .<sup>26</sup> It was concluded that intercalation adsorption of PEO happened and the adsorbed PEO takes a conformation or form of pancake shaped disk in the interlamellar region, whose radius  $R_{F2}$  was proportional to the square root of  $N$ , but was smaller than the unperturbed radius of gyration in three dimension as shown in Figure 9.

Free energy of adsorption of PEO calculated from the adsorption isotherm became more negative with increase of  $N$  and the adsorption entropy became increasingly positive as shown in Table II. Upon the intercalation adsorption of PEO, its conformation is restricted and thus entropy is reduced. Therefore, the positive entropy originates from the desorption of water molecules from the interlamella region.<sup>25 ~ 27</sup>

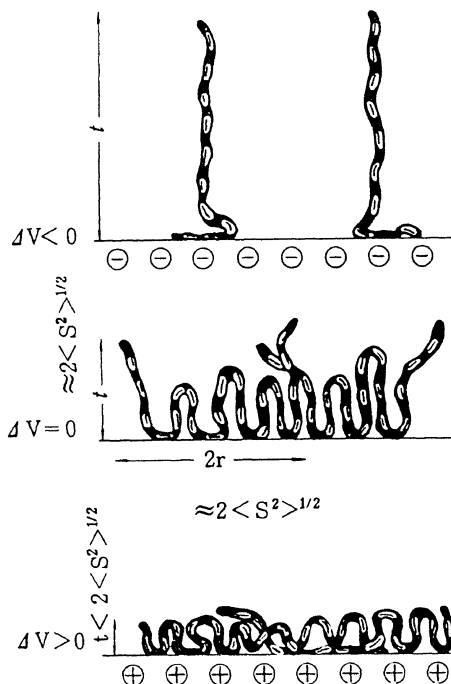


Figure 6. Models for the conformation changes of adsorbed NaPSS chains under potential variation.

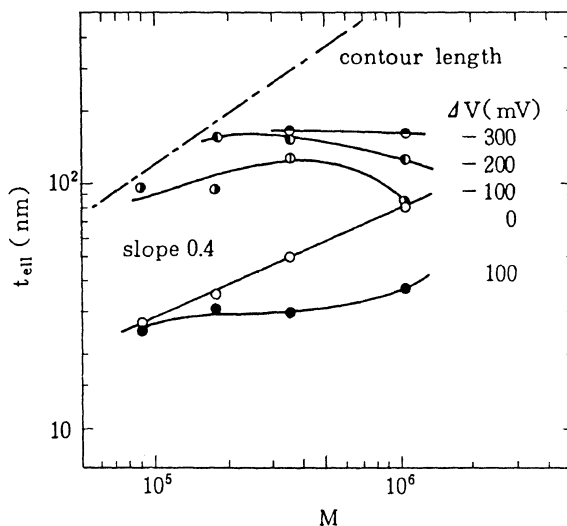


Figure 7. Double logarithmic plot of adsorbed layer thickness versus molecular weight of NaPSS in aqueous 0.1M NaCl solution.

## CONCLUSIONS

I could realize various adsorbed conformations and configurations of polymers by designing polymer structure and controlling interactions among polymers, solvents and adsorbents. In Figure 10, the exponent  $\nu$  of molecular weight dependence of the adsorbed layer thickness is summarized for various adsorbed conformations.

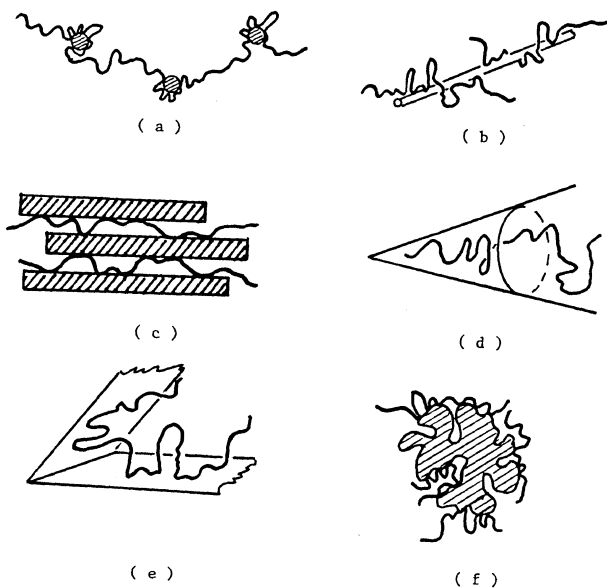


Figure 8. Adsorbed polymer chains in various geometries. (a) necklace type adsorption on colloidal sphere; (b) on a rod; (c) in slits; (d) in a cone; (e) in a wedge; (f) on a fractal surface.

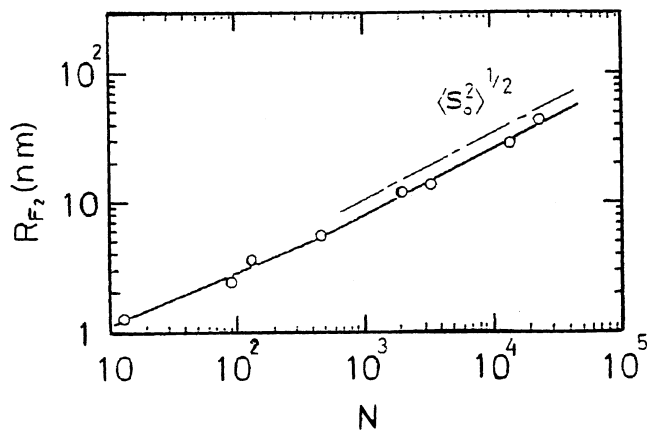


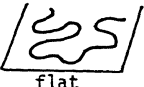
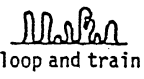

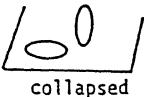
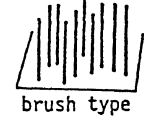
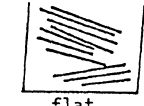
Figure 9. Chain length dependence of radius of adsorbed PEO disk ( $R_{F_2}$ ) and unperturbed radius of gyration.



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**Table II.** Non-standard thermodynamic data for the adsorption of PEO by calcium montmorillonite

$M_w$ of PEO	15°C		35°C	
	$-\Delta G_m$ cal/mol	$-\Delta G_m$ cal/mol	$-\Delta H_m$ cal/mol	$\Delta S_m$ e.u.
400	783	821	716	0.34
6,000	3385	3621	1102	7.9
20,000	4698	5140	1674	11.5

Model	Relationship between $M_w$ and Layer Thickness $t$ Adsorbance $A$		portion of adsorbed monomer units $p$
 flat	$\sim M^0$	$\sim M^0$	1
 loop and train	(Theory $\sim M^{1/2}$ ) $\sim M^0$	$\sim M^a$ $0 < a < 1$	—
 loop, train and tail	⊕ $\sim M^{1/2}$ Good solvent $\sim M^{2/5}$	$\sim M^a$ $0 < a < 1$	—
 collapsed	long or short dimension (depends on orientation)	$\sim M^{1/3}$	—
 brush type	$\sim M^1$	$\sim M^1$	$\ll 1$
 flat	$\sim M^0$	$\sim M^0$	$\sim 1$

**Figure 10.** Models for the conformation of adsorbed polymers.

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