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GLASSY STATES OF ADSORBED FLEXIBLE POLYMERS AND SPREAD POLYMER "MONOLAYERS"

K. KREMER*

*Exxon Research and Engineering Company, Corporate
Research Science Laboratories, Clinton Township,
Route 22 East, Annandale, New Jersey 08801, U.S.A.*

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RESUME

Nous proposons un mécanisme possible pour la dynamique des polymères adsorbés. On suggère qu'un état vitreux puisse exister près de la surface. On considère les propriétés conséquentes pour une couche polymérique à une interface air-liquide.

ABSTRACT

In this letter we conjecture a possible mechanism for the dynamics of irreversibly adsorbed polymers. We argue that glass-like states can exist near the surface. Subsequently, we discuss this in reference to the properties of polymers spread on a liquid air interface.

During the last few years an increasing number of experiments were performed, which deal with the irreversible adsorption of polystyrene on mica¹⁻⁴ and on metal surfaces⁵⁻⁷. These experiments deal with the forces between mica surfaces²⁻⁴, or with the total amount of polymer adsorbed^{1,5-7} and the thickness of the adsorbed layer²⁻⁷. While the results of the different approaches are quite consistent, there is very little known about the dynamics of such systems. de Gennes reported some ideas of chains creeping on the surface⁸. Terashima et al.¹ measure the surface excess of polystyrene in cyclohexane adsorbed on mica. They report, that

the amount of irreversibly adsorbed polymer, after exposing the mica to pure solvent, did not change. The adsorbed amount is independent of the original solvent concentration. These findings are in agreement with other authors^{2,5-7}. One finds that almost no polymers leave this layer and dissolve into solution. Now let us ask what might be interesting about the internal dynamics of such layers. de Gennes creeping model allows for exchanges of contacts with the surface between different segments of the chains⁸. This would allow for some chains to adsorb completely, while others could leave the surface. Indeed if one adds low molecular weight poly-

*Present address : Institut für Physik, Johannes Gutenberg-Universität,
D-6500 Mainz 1, F.R.G.

mers one can find some surface exchange²¹. In order to understand the dynamics of such layers in more detail, one needs information about their structure. Refs. 2-7 give information on both the thickness of the layers and the density profiles $\rho(z)$.

We now want to discuss the internal dynamics of irreversibly adsorbed polymers, for which the adsorption temperature is around the glass transition. It should be noted, that the polymer density near the surface is close to the melt density, where bulk polystyrene is a glass ($T_G=378K$). In the present system the density $\rho(z)$, where z is the distance from the surface, should decrease like^{10,11} (in mean field theory)

$$\rho(z) = \rho(z=\infty) \coth^2(z/R+\sigma) \quad (1)$$

This form is supported by the experiments of Ref. 10, where R is the solution radius of gyration and $\sigma \approx 0.1$. The mica force experiments impose, that $\rho(z) \approx \rho_{\text{bulk}}$ up to a certain value z_0 . z_0 is given by the distance $d = 2z_0$, where the mica sheets repel each other strongly and indicate an almost incompressible surface layer. Comparing this with the force measurements of references 2-4, it is reasonable to assume, that at the distance where the repulsion starts

$$\rho(z)/\rho(z \rightarrow 0) \approx 0(e^{-1}) \quad (2)$$

In this region the steep decrease in the density should appear. Typically this occurs at about 150Å separation of the mica, which corresponds to about 2/3 of the radius of gyration of the polymers used. (These are the data for the high surface coverage experiment. That is an experiment, where the standard amount of irreversibly adsorbed polymer is reached. The low coverage experiment has less polymer at the surface than can adsorb irreversibly.)

We know that glasses may be formed in two different ways: 1) by taking a melt and cooling it down below T_G ; or 2) by taking a solution below T_G and increasing the polymer concentration. For polystyrene in Benzene or Toluene (both are good solvents at room temperature), the glass concentration is around 85-90% polystyrene and 10-15% solvent at room temperature¹². For the θ -solvent, where the monomers already attract each other on order to compensate for the excluded volume, this should give a lower solvent concentration limit. That is in good agreement with a Monte Carlo simulation¹³, where freezing or the glass transition is analyzed in terms of the chain length and/or the plasticizer

concentration. Taking all these results into account, I think it is reasonable to consider a surface layer of about 10-20% of R_G (ref.2), where the irreversibly adsorbed chains are in a glassy state. This is a very conservative estimate. Taking into account, that many monomers are strongly bonded to the surface and that the surface introduces configurational constraints, the glassy layer may be even thicker. Of course this needs further explanation and a more detailed molecular model¹⁴, as well as experiments to check the local dynamics.

Actually there are two experiments which seem not to fit into this picture. One is the θ -solvent experiment of polystyrene⁴, but here the polymers are not strongly adsorbed as the authors find. That means that the density near the surface might be too low in order to form a glass. The chains thus can desorb into solution. The second is the adsorption of polyethyleneoxide (PEO) on mica³. There, Klein and Luckham find, that the forces between the surfaces clearly depend on the compression rates. But the glass temperature of PEO is around 233K⁹ and the measurements were performed at $T(\approx 300K) > T_G$. Such a hysteresis should not occur for the discussed PS systems. Indeed the experiments^{2,4} seem to be reversible, but now special experiment was performed up to now. For these two systems, we therefore cannot expect to find glassy states in contrast to the other one discussed. To our knowledge there do not exist similar experiments with Polybutadiene, which should show a similar effect as PEO. Another problem may occur if one wants to identify such a glassy layer. Due to the liquid part of the adsorbed layer, which is formed by chains, which only partly belong to the glassy sheet, the system might look like a gel²¹. This means that it is probably somewhat difficult to distinguish a frozen layer with a liquid top from a gel.

Now let us turn to a different system, which may show similar effects, namely spread layers of PS on an air water interface. In a recent experiment Kim and Peiffer¹⁵ spread PS from a solution onto a water surface. The solvent evaporates from the water surface. They report, that the exponent ν of the radius of gyration or the end-to-end distance ($R_G^2 \propto R^2 \propto N^{2\nu}$, N the number of bonds) remains nearly unchanged at the surface compared to the bulk. For the spread systems they find $\nu=0.6$, $T > \theta_{d=3}$, and $\nu=0.54$, $T \approx \theta_{d=3}$. This is very surprising, since the 2-d value for θ is much

lower than the 3-d value for the same solvent, as has been seen, e.g., in simulations^{16,17}. For self-avoiding walks (SAW) with nearest neighbor interaction on the cubic lattice Mazur and McCrackin find $\theta = kt/\epsilon \approx 3$ while Baumgärtner finds $\theta = 1.2$ on the square lattice. For the spread chain this means, that as long as the solvent is not evaporated, the chain in both cases tries to expand to the 2-d SAW structure, namely $\nu = 0.75$. Kim and Peiffer find $\nu = 0.54$ ($0.6, T > \theta$), while experiments on the 2-d θ -point of polymers give $\nu \approx 0.51$ ¹⁸. The results seem to indicate that the chains try to expand, but were hindered by some mechanism. A possible mechanism is due to knots. In order to understand this let us assume, that the spread θ -chain is a projection of a Gaussian coil. This means the number of knots or crossing is proportional to N (or to $N^{0.8}$ in good solvent case). Because of the flat geometry it is very improbable that two such knots can pass through one another. This certainly can lead to density fluctuations, which are fixed enough to be quasi-stable. Experiments to check this effect are underway¹⁹.

To conclude it is not clear, whether the dynamics of the extremely slow quasi stable states of the two systems considered here are governed by the same physical process. But in both cases, it is important to consider the possibility of frozen or glass-like configurations in order to rationalize the kinetic observations. Whether these quasi two dimensional frozen states can be understood in terms of conventional polymer glasses, or whether one needs a different approach should be investigated. Experiments on very thin films (a few bond lengths thick) of polymer melts are underway²⁰ and should give some insight into these questions.

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