Volume Fraction Profiles of Terminally Attached Chains

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ABSTRACT

Terminally attached or end grafted chains can exist in a variety of surface configurations. These structures can be described by the volume fraction of segments normal to the interface and depend on several factors including the graft density, the chain length and the thermodynamic interactions of the chain segments with the solvent and the interface. In this paper small-angle neutron scattering [SANS] is used to investigate these surface volume fraction profiles.

INTRODUCTION

The structure of adsorbed polymer layers, where one end of the chain is terminally attached has been described by several theoretical approaches. These include the Monte Carlo method [1], the mean field model [2] and scaling arguments [3]. The detailed structure of these layers depends strongly on the adsorbed amount or graft density. In the extreme case of high coverages a brush like regime might be expected, but at lower coverages a more parabolic or gaussian shape may be found. In a recent paper Auroy et al [4] have successfully used SANS to probe the structure of polydimethylsiloxane grafted on porous silicas. In their work they found that the adsorbed layer in a good solvent was diffuse but could still be fitted to a block model of the profile. In their paper they also found that measurements with the particles at contrast match with the solvent did not agree in detail with that obtained off contrast. In an earlier paper [5] we showed that for poly(vinyl acetate-co-alcohol) both the on and off contrast terms gave rather similar volume fraction profiles when numerically transformed. Recently a similar result was found for polystyrene adsorbed on silica [6]. The differences in these observations may be related to the relative persistence lengths of the polymers used as well as their overall molecular weight. For example it is known that for flexible polymers in solution, scaling behavior is observed over a much wider range of concentrations and molecular weights that for stiffer chains [for example see the experimental data in reference 7]. In this paper we shall discuss both the molecular weight and coverage dependence of terminally attached polystyrene chains under good solvent conditions from experiments carried out under contrast-match conditions.

TABLE 1

Molecular Weight	Adsorbed Amount/mg m^{-2}	RMS/nm
24,000 [D]	6.5	13.5
12,000 [H]	5.5	7.1
4,800 [H]	2.75	1.92

EXPERIMENTAL

The polystyrenes used were prepared by an anionic polymerization and subsequently terminally grafted onto silica [8] from dimethyl formamide. The samples were then redispersed in carbon tetrachloride. The characteristics of the samples are given in Table 1. The SANS data were obtained on the D17 instrument at the ILL Grenoble using a sample detector distance of 3.8m and a wavelength of 1.2nm. All experiments were carried out by contrast matching the particles with carbon tetrachloride with a small amount of deuterated dichloromethane.

RESULTS AND DISCUSSION

Figure 1 shows the scattering profiles expected from four different volume fraction models for terminally attached chains. These model profiles are shown in Figure 2. As can be seen the profiles with a discontinuous behavior produce oscillations in the scattering. The smoother profiles give rather smaller variations in intensity. In a real system polydispersity will effectively smooth and damp these oscillations particularly for the block and parabolic profiles. Figure 3 shows the experimental scattering obtained from deuterated 24,000 polystyrene adsorbed on silica in carbon tetrachloride at a coverage of 6.5 mg/m^2. The scattering does not have any rapid oscillations but does show a distinctive wave at a $Q \sim 0.02$nm^{-1}. The solid lines are fits to this data using the various models for the volume fraction profile given in Figure 2. The actual volume fraction profiles resulting from these fits are shown in Figure 4. The best fit judged visually and also from the χ^2 statistic is the gaussian profile, which has a maximum away from the interface. Also shown in Figure 4 is the profile obtained by a numerical inversion of the same data [5]. The agreement between these two approaches is good and shows that the profile with a distinct maximum best represents the experimental scattering. The reason for the effective repulsion of the polystyrene segments from the interface is due to the sample preparation procedure. Dimethyl formamide, [DMF] which was the grafting solvent, is strongly adsorbed onto the silica surface. In effect DMF is a displacer as polystyrene does not adsorb onto silica from solution in DMF [8]. The subsequent solvent exchange with carbon tetrachloride does not remove the layer of DMF as evidenced by FTIR. Both the MC and mean field models for terminally attached and non-returning tails [i.e. χ_s, the net segment/solvent exchange enthalpy is less than the critical value for adsorption] predict a maximum in the volume
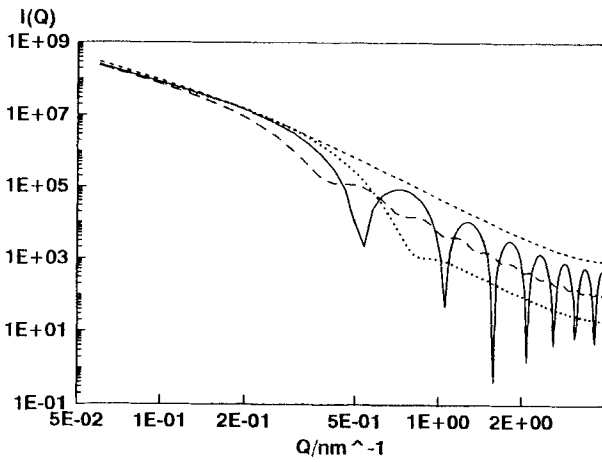
Figure 1   Small-angle Scattering from various volume fraction profiles
              --- exponential, ...gaussian _____ block, _ _ parabola.
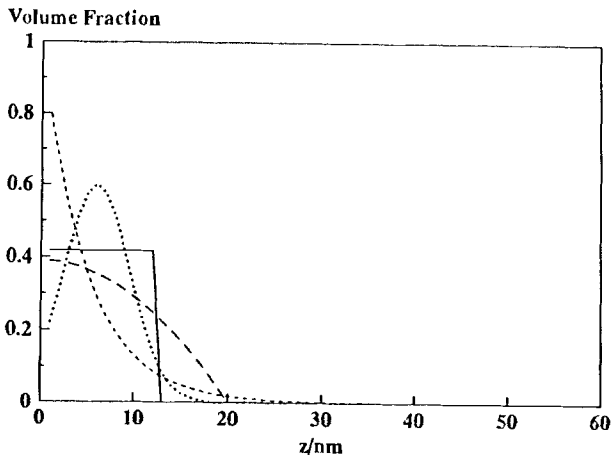
Figure 2   Volume fraction profiles for the scattering shown in Figure 1
              --- exponential, ...gaussian _____ block, _ _ parabola.
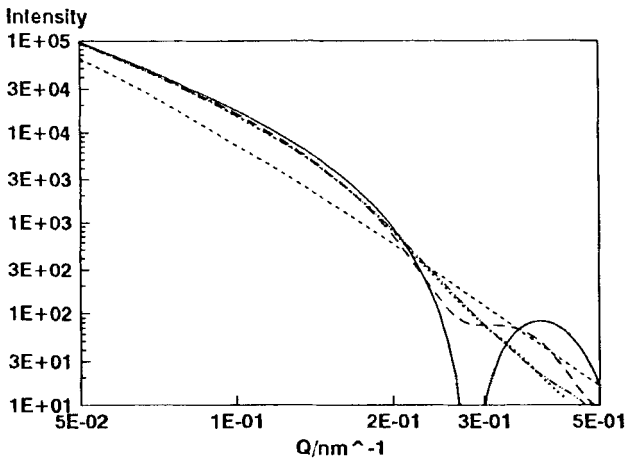
Figure 3   Fits to the experimental scattering from 24,000 deuterated
             polystyrene on silica [see Table 1] from the volume fraction profiles
             shown in Figure 4. --- exponential, _. . _ gaussian _____ block, _ _
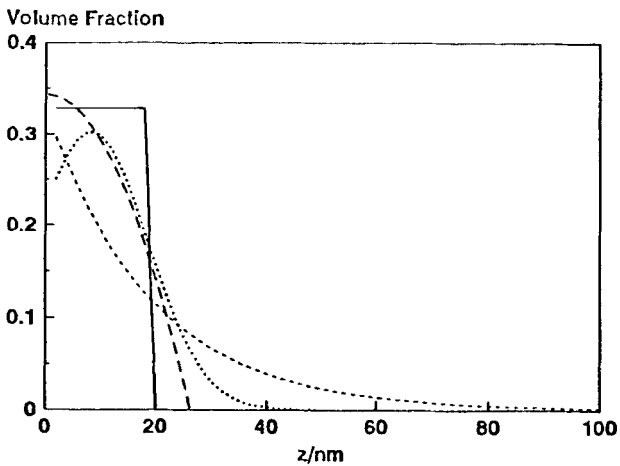   parabola, ... experimental data.

Figure 4   Volume fraction profiles obtained from the fits to the 24,000
             polystyrene data shown in Figure 3 --- exponential, _. . _ gaussian
             _____ block, _ _ parabola.

Volume Fraction

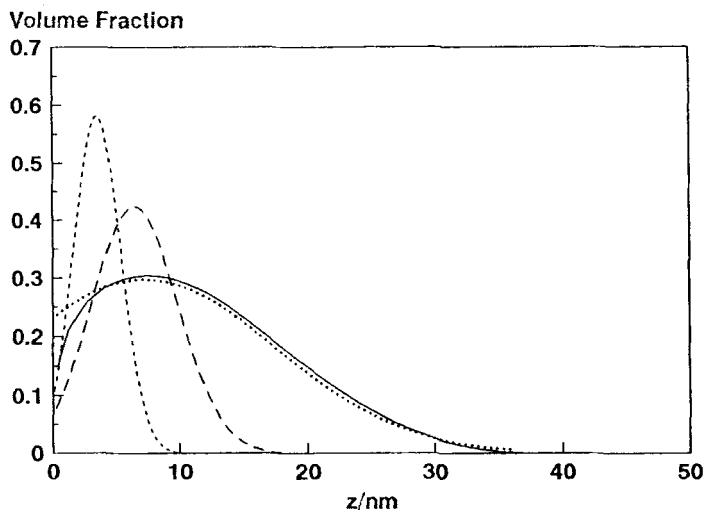

Figure 5   Gaussian fits to the scattering from polystyrene terminally attached on silica: - - - 4,800 _ _ 12,000 . . . . 24,000 _____ 24,000 by numerical inversion.

fraction profile [1]. In this system therefore there is no evidence of a step like profile like regime. The data of Auroy et al [4] however have been fitted successfully to a step profile, with a polydispersity factor. The samples used however were of a higher grafted amount than those in the present study. Figure [5] shows profiles obtained by fitting gaussian profiles to the scattering obtained from two further samples that were prepared in the same way except that in these cases the polymer was protonated [Table 1]. This unfortunately leads to a much poorer contrast between the polymer and the contrast-matched particle and solvent and a concomitant reduction in the statistics of the data. In both these cases the difference in the χ^2 statistic between the various models was rather small though the exponential fit was inferior in all cases. This is in marked contradistinction to a physically adsorbed polymer where the volume fraction profiles are close to being exponential in shape [9]. These results emphasize that very good statistics are required in these data if one is to be able to distinguish between models of the adsorbed layer. A further discussion of this point is deferred to a subsequent publication [6]. The profiles given in Figure 6 can be used to obtain the RMS thickness of the layers and these are also given in Table 1. The results are consistent, within experimental error, with the brush scaling prediction using the modified form given by Klein [10]

$$\delta_{RMS} \sim N^{0.6}$$

CONCLUSIONS

The shape of the volume fraction of a terminally attached chain, which does not physically adsorbed can be described rather well by a shifted gaussian function. This has been confirmed by comparing both a numerical inversion of the data with a non-linear least squares fit for a deuterated polystyrene attached to a silica particle. Lower molecular weight samples however did not have sufficiently good statistics to make it possible to give an unambiguous statement regarding the profile shape. The RMS thicknesses calculated from the profiles, assuming a gaussian profile shape fit the Alexander-de Gennes model and show that the chains are extended normal to the interface as expected.

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