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Adsorption of Polymer from Solution to Solid Surface: Effect of Polydispersity

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Introduction

Polymers are used to modify the properties of solid surfaces in a variety of industrial applications, e.g., flocculation, colloid stabilization, lubrication, drag reduction, and biocompatibilization. Most conventional methods of polymer synthesis yield a polydisperse product. From the standpoint of economy, it is desirable to use this product as such, instead of separating it into narrower molecular weight fractions. However, in such situations, the molecular weight distribution (MWD) in the adsorbed polymer layer can be significantly different from that in the feed solution. It has been observed that longer chains adsorb preferentially over shorter ones.[1,2] Since the extent to which some surface properties are modified depends strongly on the lengths of the adsorbed chains, polydispersity in the feed, beyond a certain limit, may be undesirable. For a priori estimation of this limit, one needs a model to predict how polymer chains of different lengths are distributed between the solid surface and the solution in contact with it and also obtain the configurational statistics of adsorbed chains, which would help in determining the characteristics of the adsorbed layer.

The lattice-based theoretical model, developed by Scheutjens and Fleer,[3] has been in use for predicting the molecular weight distribution of the polymer in the adsorbed state.[4−7] However, there are two lacunae of this model. First, it is computationally very intensive. The model requires that the connectivity equation be solved (in the form of the recurrence relationships) separately for each representative chain of the distribution. The intensiveness of the computation is, therefore, proportional to the product of the square of chain length, the number of lattice layers, and the number of representative chains selected for the simulation. To limit the intensiveness of the computation, it is necessary to discretize the distribution of chains into a manageably small number of discrete groups, with a single chain representing each group. This introduces a certain amount of coarseness in the simulation. Roefs et al.[6] have modified the recurrence relationships and thereby significantly reduced the amount of computation which was, otherwise, needed in the previous version of the procedure.[4,5] However, the extent of this reduction is quantitative rather than qualitative; i.e., the dependence of the computational intensiveness on the chain length, number of lattice layers, and the number of chains remains unchanged. Second, the efficacy of the lattice-based model, for quantitative prediction, has not been demonstrated. The comparisons so far presented in the literature[6] are only qualitative in nature.

Apart from the lattice theory, the models based on the continuum form of the mean field theory[8,9] and the scaling theory[9] have also been used to account for the effect polydispersity. Although these models are semianalytical in nature and are easy to use, they have been derived under restrictive approximations and hence are limited in their applicability.

In the present work, we have extended the continuum model,[10] developed earlier for the adsorption of monodisperse polymer, to the adsorption of polydisperse polymer. The polydispersity effect has been incorporated in the form of two integrals (defined by eqs 22 and 23) in the finite element formulation of the equation describing the chain connectivity. These integrals can be analytically evaluated for most commonly used continuous probability density functions for the chain length distribution. Only a small amount of extra computational effort is, therefore, required to account for the effect of polydispersity. The intensiveness of the computation is proportional to the square of the number of finite elements (approximately 20) used to discretize the interfacial region but does not depend on either the chain length or the nature of the distribution. Thus, there is a qualitative reduction in the computational efforts over the Roefs et al.[6] procedure. Moreover, the theory can quantitatively predict the molecular weight distribution as is demonstrated with reference to the reported experimental data on adsorption of polydisperse polystyrene on silica from two different solvents, viz. carbon tetrachloride and cyclohexane.

The Model

The model presented here is an extension of the previous one described in detail elsewhere.[10] Consider the solution of volume V containing N chains of a flexible homopolymer species, p, in a monomeric solvent species, s, in equilibrium with a plane solid surface, having area A. The degree of the polydispersity of the polymer is expressed in the form of the number density function, $p(r)$, where $p(r)\,\mathrm{d}r$ represents the fraction of the total number of chains having the number of Kuhn segments between r and $r + \mathrm{d}r$, the length of each Kuhn segment being equal to l. The mean field theory is used to describe the configurational statistics of the polymer chain in the interfacial region. It is assumed that the adsorbed layer of the polymer extends in z-direction from $z = 0$ (surface) up to $z = d$. The sample polymer chain is viewed as a freely jointed bead-link chain kept in the mean field produced by the rest of the polymer chains and the solvent molecules. The polymer−surface and the solvent−surface interaction potentials are assumed to be localized only at the surface. The adsorbed material (solvent and polymer) forms the surface phase. The surface phase (denoted by *) is located at $z = 0$ and is assumed to have zero thickness. The connectivity of a chain having r Kuhn segments is described by the following version of the random flight model:

$$\frac{1}{r}\frac{\partial G_{\mathrm{p}}(\hat{z},\hat{q})}{\partial \hat{q}} = \frac{l^2}{6d^2}\frac{\partial^2 G_{\mathrm{p}}(\hat{z},\hat{q})}{\partial \hat{z}^2} + [1 - \mathrm{e}^{u_{\mathrm{p}}(\hat{z})/kT}]G_{\mathrm{p}}(\hat{z},\hat{q}) \qquad (1)$$

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The initial and the boundary conditions used are

$$G_{\mathrm{p}}(\hat{z},0) = \mathrm{e}^{u_{\mathrm{p}}(\hat{z})/kT} \tag{2}$$

$$G_{\mathrm{p}}(1,\hat{q}) = 1 \tag{3}$$

$$\frac{1}{r}\frac{\partial G_{\mathrm{p}}(0,\hat{q})}{\partial \hat{q}} = (1 + 2\mathrm{e}^{(u_{\mathrm{p}}(0)-u^*{}_{\mathrm{p}})/kT})^{-1}\left[\frac{l}{2d}\frac{\partial G_{\mathrm{p}}(\hat{z},\hat{q})}{\partial \hat{z}}\bigg|_{\hat{z}=0} + G_{\mathrm{p}}(0,\hat{q})\{1 - 2\mathrm{e}^{u_{\mathrm{p}}(0)/kT} + 2\mathrm{e}^{(u_{\mathrm{p}}(0)-u^*{}_{\mathrm{p}})/kT}\}\right] \tag{4}$$

In the above equation, $G_{\mathrm{p}}(\hat{z},\hat{q})$ is the probability, relative to the bulk solution, of finding the end of a subchain of contour length q at location z. The terms $\hat{q}$ ($=q/rl$) and $\hat{z}$ ($=z/d$) represent the normalized forms of q and z, respectively, and $u_{\mathrm{p}}(\hat{z})$ represents the potential of the Kuhn segment at location $\hat{z}$, whereas $u^*{}_{\mathrm{p}}$ represents the corresponding potential in the surface phase.

The concentration of the polymer in the interfacial region is expressed as volume fraction ϕ_{p}. The volume fraction density, $\phi_{\mathrm{p}}(\hat{z},r)$, of the chains of length r, at location $\hat{z}$ in the interfacial region is related to bulk volume fraction density $\phi_{\mathrm{p}}^{\mathrm{b}}(r)$ by the following equation:

$$\frac{\phi_{\mathrm{p}}(\hat{z},r)}{\phi_{\mathrm{p}}^{\mathrm{b}}(r)} = \mathrm{e}^{u_{\mathrm{p}}(z)/kT}\int_0^1 G_{\mathrm{p}}(\hat{z},\hat{q})\, G_{\mathrm{p}}(\hat{z},1-\hat{q})\, \mathrm{d}\hat{q} \tag{5}$$

The volume fraction of the polymer at any location z in the interfacial region is given by

$$\phi_{\mathrm{p}}(\hat{z}) = \int_0^\infty \phi_{\mathrm{p}}(\hat{z},r)\, \mathrm{d}r \tag{6}$$

In the surface phase, which is two-dimensional, concentrations are expressed in terms of the area fraction $\varphi^*{}_{\mathrm{p}}$. The area fraction density can be obtained using the following equation

$$\varphi^*{}_{\mathrm{p}}(r) = \mathrm{e}^{(u_{\mathrm{p}}(0)-u^*{}_{\mathrm{p}})/kT}\phi_{\mathrm{p}}(0,r) \tag{7}$$

where $\phi_{\mathrm{p}}(0,r)$ is computed from eq 5 by substituting $\hat{z} = 0$. The area fraction is given by

$$\varphi^*{}_{\mathrm{p}} = \int_0^\infty \varphi^*{}_{\mathrm{p}}(r)\, \mathrm{d}r \tag{8}$$

The potentials in the interfacial region and the surface phase can be expressed as[11]

$$\frac{u_{\mathrm{p}}(z)}{kT} = \frac{v_{\mathrm{p}}}{v_{\mathrm{s}}}\left[\chi(1 - 2\phi_{\mathrm{p}}) - \chi^{\mathrm{b}}(1 - 2\phi_{\mathrm{p}}^{\mathrm{b}}) + (1 - \phi_{\mathrm{p}})\phi_{\mathrm{p}}\frac{\partial\chi}{\partial\phi_{\mathrm{p}}} - (1 - \phi_{\mathrm{b}}^{\mathrm{p}})\phi_{\mathrm{b}}^{\mathrm{p}}\frac{\partial\chi}{\partial\phi_{\mathrm{p}}^{\mathrm{b}}} - \ln\left(\frac{1 - \phi_{\mathrm{p}}}{1 - \phi_{\mathrm{p}}^{\mathrm{b}}}\right)\right] \tag{9}$$

$$\frac{u^*{}_{\mathrm{p}}}{kT} = \frac{v_{\mathrm{p}}}{v_{\mathrm{s}}}\left[\chi'(1 - 2\varphi^*{}_{\mathrm{p}}) - \chi^{\mathrm{b}}(1 - 2\phi_{\mathrm{b}}^{\mathrm{b}}) + (1 - \varphi^*{}_{\mathrm{p}})\varphi^*{}_{\mathrm{p}}\frac{\partial\chi'}{\partial\varphi^*{}_{\mathrm{p}}} - (1 - \phi_{\mathrm{b}}^{\mathrm{p}})\phi_{\mathrm{b}}^{\mathrm{p}}\frac{\partial\chi}{\partial\phi_{\mathrm{b}}^{\mathrm{p}}} - \ln\left(\frac{1 - \varphi^*{}_{\mathrm{p}}}{\phi_{\mathrm{s}}^{\mathrm{p}}}\right)\right] - \chi^* \tag{10}$$

These equations take into account the possible variation of the Flory–Huggins χ-parameter with the concentration of the polymer. The χ-parameter in the bulk is denoted by χ^{b} and that in the surface phase by χ'. The term χ^* is the polymer–surface affinity parameter and represents the affinity of the polymer for the surface, relative to that of the solvent molecule.

Equations 1, 3, and 4 can be cast into a set of linear ordinary differential equations in $\hat{q}$ by discretizing the $\hat{z}$ domain into finite elements. We use the following interpolation form:

$$G_{\mathrm{p}}(\hat{z},\hat{q}) = \sum_{k=1}^{2M+1} N_k(\hat{z})\, G_{\mathrm{p}}(\hat{z}_k,\hat{q}) \tag{11}$$

$\hat{z}_k$ is the location of the finite element node k and $N_k(\hat{z})$ is the interpolation polynomial corresponding to node k. The resulting matrix form of the equations is

$$\frac{1}{r}\vec{E}\frac{\mathrm{d}\vec{G}_{\mathrm{p}}}{\mathrm{d}\hat{q}} = \vec{C}\vec{G}_{\mathrm{p}} + \vec{d} \tag{12}$$

where $\vec{G}_{\mathrm{p}}$ is the column vector of the values of G_{p} at the nodes. The matrices $\vec{C}$ and $\vec{d}$ are as defined in the previous paper,[9] and matrix $\vec{E}$ is related to matrix $\vec{B}$ of the previous paper by

$$\vec{B} = \frac{1}{r}\vec{E} \tag{13}$$

Equation 12 can be solved subject to the initial condition 2 to yield

$$\vec{G}_{\mathrm{p}} = \vec{U}(\vec{\mathrm{e}}^{rq\Lambda})\vec{U}^{-1}[\vec{G}_{\mathrm{p,f}} + \vec{C}^{-1}\vec{d}] - \vec{C}^{-1}\vec{d} \tag{14}$$

where $\vec{\Lambda}$ is the diagonal matrix of eigenvalues satisfying the generalized eigenvalue problem

$$\vec{C}\vec{u}_i = \lambda_i\vec{E}\vec{u}_i \tag{15}$$

$\vec{U}$, in eq 14 is the matrix having the eigenvectors $\vec{u}_i$ as its columns.

Using eqs 5 and 14, the following equation for the volume fraction density at location $\hat{z}$ is obtained

$$\phi_{\mathrm{p}}(\hat{z}_j,r) = \phi_{\mathrm{p}}^{\mathrm{b}}(r)\mathrm{e}^{u_{\mathrm{p}}(\hat{z}\hat{j})/kT}\left[\sum_{m=1}^{2M}\sum_{n=1,m}^{2M} U_{jm}U_{jn}v_m v_n\left(\frac{\mathrm{e}^{r\lambda_m} - \mathrm{e}^{r\lambda_n}}{r(\lambda_m - \lambda_n)}\right) + \sum_{m=1}^{2M} U_{jm}{}^2\, v_m{}^2\mathrm{e}^{r\lambda_m} - 2w_j\sum_{m=1}^{2M} U_{jm}v_m\left(\frac{\mathrm{e}^{r\lambda_m} - 1}{r\lambda_m}\right) + w_j{}^2\right] \tag{16}$$

The volume fraction density in the bulk is given by

$$\phi_{\mathrm{p}}^{\mathrm{b}}(r) = v_{\mathrm{p}}Nrp(r)/V \tag{17}$$

and is related to the volume fraction $\phi_{\mathrm{p}}^{\mathrm{b}}$ by the following equation:

$$\frac{\phi_{\mathrm{p}}^{\mathrm{b}}(r)}{\phi_{\mathrm{p}}^{\mathrm{b}}} = \frac{rp(r)}{\int_0^\infty rp(r)\, \mathrm{d}r} \tag{18}$$

We make use of eq 18 to eliminate $\phi_p^b(r)$ from eq 16 and obtain

$$\phi_p(\hat{z}_j,r) = \frac{\phi_p^b p(r) e^{u_p(\hat{z})/kT}}{\bar{r}} \times \left[\sum_{m=1}^{2M} \sum_{n=1,m}^{2M} U_{jm} U_{jn} v_m v_n \frac{e^{r\lambda_m} - e^{r\lambda_n}}{\lambda_m - \lambda_n} + \sum_{m=1}^{2M} U_{jm}{}^2 v_m{}^2 r e^{r\lambda_m} - 2w_j \sum_{m=1}^{2M} U_{jm} v_m \frac{e^{r\lambda_m} - 1}{\lambda_m} + r w_j{}^2\right] \quad (19)$$

where $\bar{r}$ is the number-averaged chain length of the polymer

$$\bar{r} = \int_0^\infty r p(r)\, dr \quad (20)$$

Integration of eq 19 with respect to r yields the following expression for the volume fraction profile of the polymer.

$$\phi_p(\hat{z}_j) = \frac{1}{\bar{r}} \phi_p^b(r) e^{u_p(\hat{z}_j)/kT} \left[\sum_{m=1}^{2M} \sum_{n=1,m}^{2M} U_{jm} U_{jn} v_m v_n \frac{I_1(\lambda_m) - I_1(\lambda_n)}{\lambda_m - \lambda_n} + \sum_{m=1}^{2M} U_{jm}{}^2 v_m{}^2 I_2(\lambda_m) - 2w_j \sum_{m=1}^{2M} U_{jm} v_m \frac{I_1(\lambda_m) - 1}{\lambda_m} + r w_j{}^2\right] \quad (21)$$

where

$$I_1(\lambda_m) = \int_0^\infty e^{r\lambda_m} p(r)\, dr \quad (22)$$

and

$$I_2(\lambda_m) = \int_0^\infty r e^{r\lambda_m} p(r)\, dr \quad (23)$$

Note that $I_1(\lambda_m)$ and $I_2(\lambda_m)$ and are related to each other by the following equation:

$$I_2(\lambda_m) = \frac{dI_1(\lambda_m)}{d\lambda_m} \quad (24)$$

The volume fraction profile of the polymer computed from eq 21 can be used in the self-consistent-field computations in the manner identical to that used in the case of monodisperse polymer. This means that only additional step required at each cycle of the iteration is the evaluation of the integrals given by eqs 22 and 23. In general, these integrals need numerical evaluation. However, for many common continuous distributions, these integrals can be analytically evaluated as seen from Table 1. The distributions illustrated here are Flory–Schultz, Flory–Zimm, and Gaussian.

After completion of the self-consistent-field computation, the equilibrium surface excess mass density $\Gamma(r)$ can be computed by the using the following equation:

$$\Gamma(r) = \frac{M_l l}{N_{av} v_p} \left[\int_0^1 (\phi_p(\hat{z},r) - \phi_p^b(r))\, d\hat{z} + \frac{v_s}{a_s l}(\varphi^*{}_p(r) - \phi_p^b(r))\right] \quad (25)$$

Here, M_l is the molecular weight of the Kuhn segment, N_{av} is the Avogadro number, and a_s is the area occupied by solvent molecule in the surface phase.

The following balance equation for the polymer volume relates composition of the feed, the supernatant solution, and the adsorbed layer.

$$V\phi_p^f(r) = V\phi_p^b(r) + \frac{N_{av} v_p}{M_l} \Gamma(r) A \quad (26)$$

where V is the volume of the solution and A is the surface area of the solid. $\phi_p^f(r)$ is the volume fraction density of the polymer in the feed solution, and $\phi_p^b(r)$ is that in the supernatant solution in the equilibrated system. The term $N_{av}v_p/M_l$ converts the polymer mass in the adsorbed layer to the corresponding volume.

Validation of the Model

The model has been validated using the experimental data reported by Vander Linden and Van Leemput[2] on adsorption of polystyrene, at 308 K, from cyclohexane (bad solvent) and carbon tetrachloride (good solvent) on silica (Aerosil130). The molecular weight distributions of the polystyrene in the feed and the supernatant solution are determined using a gel permeation chromatograph provided with a refractometer for measuring the concentration of polystyrene in the eluent, based on difference in the refractive index of the polymer and the eluting solvent. The experimental data are reported by the authors in the form of plots of normalized refractometer response vs elution volume. The authors have obtained the relation between elution volume and molecular weight by independent calibration using narrow molecular weight standards of polystyrene. This allows the abscissa of the plot to be converted from elution volume to molecular weight. Since the refractometer response is directly proportional to the volume fraction density and the area under the volume fraction density vs molecular weight curve should be unity, it is possible to convert the ordinate from normalized refractometer response to the volume fraction density $\phi_p(M_p)$. These data are represented by points in Figures 1–3 and are used for the validation of our model.

The values of the parameters required for the simulation have been obtained as follows. The correlation

Table 1. Expressions for Integrals I_1 and I_2 (See Eqs 22 and 23) for Some Common Chain Length Distributions

distribution	I_1	I_2
Flory–Schultz $p(r) = (1/\bar{r})e^{-r/\bar{r}}$, $0 \le r \le r_{max}$	$[1/(\bar{r}\lambda_m - 1)](e^{(r_{max}/\bar{r})(\bar{r}\lambda_m - 1)} - 1)$	$[r^{max}/(\bar{r}\lambda_m - 1)]e^{(r_{max}/\bar{r})(\bar{r}\lambda_m - 1)}$
Flory–Zimm $p(r) = [a^a/\bar{r}\Gamma(a)](r/\bar{r})^{a-1}e^{-a(r/\bar{r})}$	$(1 - \lambda_m\bar{r}/a)^{-a}$	$\bar{r}(1 - \lambda_m\bar{r}/a)^{-a-1}$
Gaussian $p(r) = 1/[(2\pi)^{1/2}\sigma]e^{-(r-\bar{r})^2/2\sigma^2}$	$^1/_2 e^{B/2\sigma^2}[1 + \mathrm{erf}(A/\sqrt{2}\sigma)]$ $A = \sigma^2\lambda_m + \bar{r}$; $B = A^2 - \bar{r}^2$	$[1/(2\pi)^{1/2}]e^{\bar{r}^2/2\sigma^2} + (A/2)e^{B/2\sigma^2}[1 + \mathrm{erf}(A/\sqrt{2}\sigma)]$

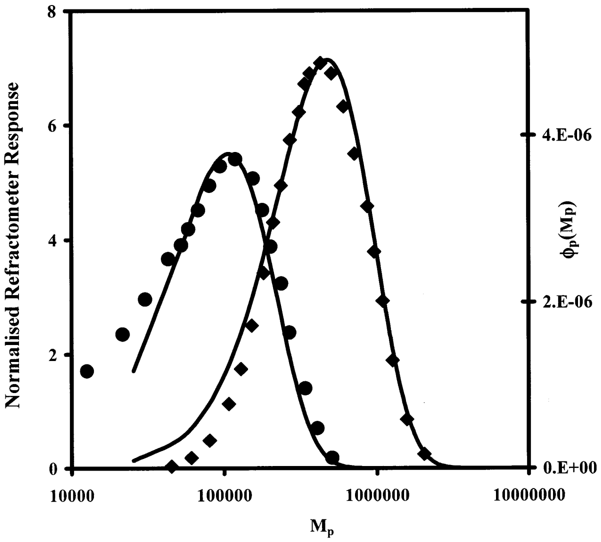

Figure 1. Adsorption of PS on Aerosil 130 from CCl_4.[2] The solid curves correspond to the simulation, and the points represent the experimental results. Experimental data: ϕ_p^b $=1.56378 \times 10^{-3}$, $\Gamma = 1.12$ mg m^{-2}. Estimated values of Flory–Zimm parameters for the supernatant solution: $\bar{r} = 208$, $a = 1.75$. Estimated values of other model parameters: $V/Al = 112$, $f = 0.323$.

length of the polymer chain l is estimated from its radius of gyration, R_g, for PS under Θ conditions.[12]

$$R_g\,(\mathrm{nm}) = 0.0290\sqrt{M_p} \tag{27}$$

The correlation length is related to R_g by the following equation:

$$l\,(\mathrm{nm}) = \frac{6{R_g}^2 M_m}{n_b M_p l_b} \tag{28}$$

where M_m is the molecular weight of the repeat unit of polystyrene (=104), n_b is the number of backbone (C–C) bonds per monomer (=2), and l_b is the length of the backbone bond (0.154 nm). The estimated value of l from eq 28 is 1.704 nm. The number of monomer units per Kuhn segment (of length l) is 5.532, and its molecular weight, M_l, is 579.5.

The volume fraction densities $\phi_p(M_p)$ and $\phi_p(r)$ are related by the relation $\phi_p(M_p)\,dM_p = \phi_p(r)\,dr$, which on rearrangement gives

$$\phi_p(r) = \phi_p(M_p) M_l \tag{29}$$

The above relation allows us to interconvert one form of the density function to the other.

The ratio of volume of polymer segment to that of solvent molecule is computed from the density of amorphous polymer (=1050 kg m^{-3})[13] and the solvent (779 kg m^{-3} for cyclohexane and 1595 kg m^{-3} for carbon tetrachloride). This yields the v_p/v_s ratio for PS–CH system as 5.07 and that for PS–CCl_4 system as 5.62.

The Flory–Huggins χ-parameter for the PS –CCl_4 system is reported at 298 K to be 0.396.[14] Because of the lack of data at 308 K, the same value of χ is used. For PS–CH system, χ is reported in the form of the following equation[15–17]

$$\chi = \chi_0(1 + p_1\phi_p + p_2{\phi_p}^2)\left(1 + \frac{k'}{r}\right) \tag{30}$$

where, at 308 K, the constants of the equation are $\chi_0 = 0.498$, $p_1 = 0.6$, $p_2 = 0$, and $k' = -0.8$. The χ-parameter in the above equation is derived by fitting the Flory–Huggins equation to experimental measurement of μ_s, the chemical potential of the solvent (CH) in the solution.

$$\frac{\mu_s}{RT} = \ln(1 - \phi_p) + \left(1 - \frac{v_s}{r v_p}\phi_p\right) + \chi{\phi_p}^2 \tag{31}$$

For concentration-dependent χ, the correct expression for μ_s is

$$\frac{\mu_s}{RT} = \ln(1 - \phi_p) + \left(1 - \frac{v_s}{r v_p}\phi_p\right) + \chi{\phi_p}^2 - {\phi_p}^2(1 - \phi_p)\frac{\partial\chi}{\partial\phi_p} \tag{32}$$

Equation 30 can be corrected to make it consistent with eq 32. The corrected form is

$$\chi = \chi_0\left[1 + \left(\frac{3p_1 + p_2}{6}\right)(1 + \phi_p) + \frac{p_2{\phi_p}^2}{3}\right]\left(1 + \frac{k'}{r}\right) \tag{33}$$

The constants in the above equation are same as those in eq 30. This equation is used for the subsequent analysis. Since the values of χ', the χ-parameter in the surface phase, are not available, they are estimated using eq 33, in which χ is replaced by φ^*_p. The values of χ^*, the surface affinity parameter, reported in the literature, for adsorption of PS on silica from cyclohexane is[14] 1.9 and that from CCl_4 is[18] 1.1.

The simulation is performed as follows. The Flory–Zimm form of the distribution of chain lengths in the supernatant solution is assumed. This distribution has two parameters, viz. $\bar{r}$ and a, which are fitted to the experimentally obtained distribution. The surface excess density of polymer $\Gamma(r)$ is then determined using self-consistent-field calculation, in conjunction with eq 25. The volume fraction density of PS in the feed solution is determined using eq 26 and is compared with the experimental density to evaluate the efficacy of the technique.

The unknown parameter in the model is a_s, the area occupied by one molecule of solvent on the surface of the solid. This area determines the amount of the polymer in the surface phase (second term of eq 25) and consequently the total adsorbed amount. The area, a_s, can be related to v_s, the volume of solvent molecule, by the following equation

$$a_s = f{v_s}^{2/3} \tag{34}$$

where f is a measure of the degree of packing of the solvent molecule in the surface phase. Since v_s is known, a_s can be quantified in terms of f. The value of f is estimated so as to obtain exact match between the predicted and the reported[2] values of the surface excess Γ.

For evaluating ϕ_p^f from eq 26, we need the V/A. This quantity can be expressed in dimensionless form as V/Al. It depends on the loading of the adsorbent. Vander Linden and Van Leemput[2] have not reported the values of the adsorbent loading. The value of V/Al in a given experiment is estimated so that the location of the peak

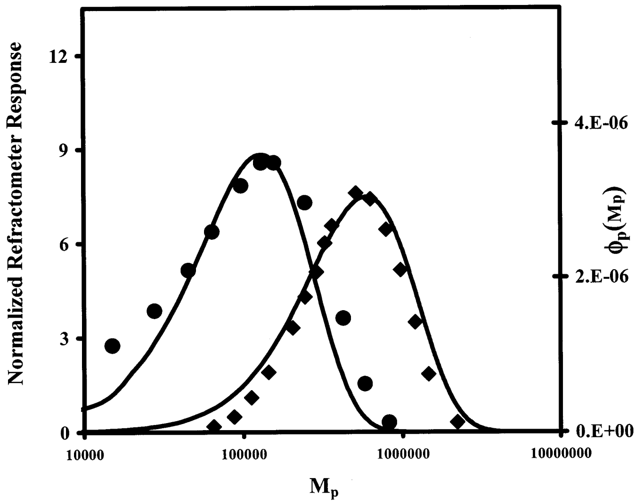

Figure 2. Adsorption of PS on Aerosil 130 from CCl_4.[2] $\phi_p^b = 1.9582 \times 10^{-3}$, $\Gamma = 1.13$ mg m^{-2}. Estimated values of the Flory–Zimm parameters: $\bar{r} = 251$, $a = 1.5$. Estimated values of the other parameters: $V/Al = 137$, $f = 0.323$.

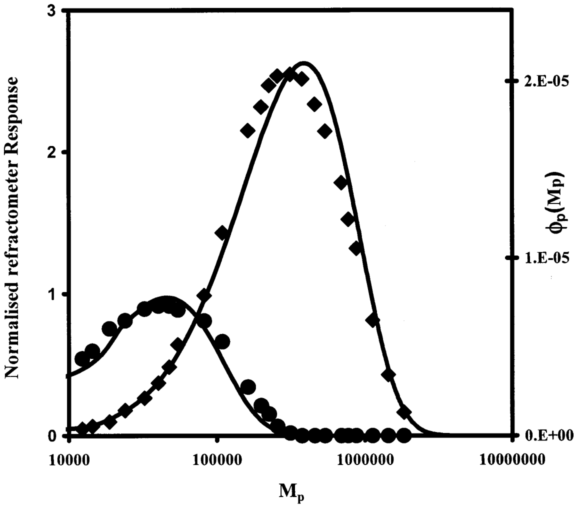

Figure 3. Adsorption of PS on Aerosil 130 from cyclohexane.[2] $\phi_p^b = 1.53 \times 10^{-3}$, $\Gamma = 2.34$ mg m^{-2}. Estimated values of the Flory–Zimm parameters: $\bar{r} = 85$, $a = 0.85$. Estimated values of the other parameters: $V/Al = 42.5$, $f = 0.540$.

of the estimated feed MWD matches with that of the experimental distribution.

The simulation procedure is the same as that described in the previous paper.[10] The number of the quadratic finite elements used for the simulation was 20. Simulations were conducted on a HP workstation U 9000/785. The CPU time required to obtain a complete density distribution curve was less than 150 s.

Figures 1 and 2 present the comparison between the experimental data and the simulation for the PS–CCl_4 system, whereas Figure 3 is that for the PS–CH system. In each figure, the curve to the left corresponds to the supernatant solution and the one to the right corresponds to the absorbed layer. The experimental data are represented by the points and the simulation results by solid lines. The estimated values of the parameters are also listed in the figures. It is seen that the simulated curves fit the experimental data reasonably well. The deviation at the lower molecular weight range is mainly due to the fact that the Flory–Zimm model does not fit the MWD of the supernatant solution in this range.

The estimated value of f is the same (=0.323) in Figures 1 and 2, which is expected since both refer to the same system (PS–CCl_4), whereas $f = 0.540$ for the system PS–CH. That the values of f are less than unity is indicative of the fact that the molecules are more closely packed on the silica surface than in the solution.

Conclusions

The technique presented here is seen to be significantly more efficient than those presently available. Moreover, it correctly quantifies the effect of polydispersity on adsorption. Considering that in most practical situations the polymer is present in the solution in the polydisperse state, an accurate and efficient procedure for prediction of MWD of the polymer in adsorbed layer is needed, so that the adsorbed layer characteristics can be accurately estimated. The present model is expected to fulfill these needs.

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