(Figure 6). Since the Brønsted relationship was able to quantitatively account for the PEI-D-NH_2-HCl pH dependence of PNPA esterolysis, it is reasonable to apply the relationship to the above reactions of poly(4-vinylpyridine) (Figure 7) and poly[4(5)-vinylimidazole] (Figure 8). As in the case of the PEI-D-NH_2-HCl reaction with PNPA[1] the Brønsted plots are linear. Note that the poly[4(5)-vinylimidazole] Brønsted slope, 0.8, is precisely that expected from the portion of the small-molecule imidazole plot also shown in Figure 6. The cooperative effect proposed for the polyimidazole esterolyses thus seems unwarranted.[2,12]

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Polymer Solutions near an Interface. 1. Adsorption and Depletion Layers

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ABSTRACT: We construct first the equilibrium concentration profiles for a polymer solution near a solid wall (or near the free surface). The wall is characterized by a certain "free energy of sticking", γ_1, which is negative for adsorption and positive for a repulsive surface. We are concerned with the case where γ_1 (per monomer) is small, but where the energy *per chain* is large. (1) For the attractive case (with a good solvent), we find a remarkable, *self-similar* form for the profile which is essentially independent of the bulk concentration. Most monomers are confined in a region of thickness $D \sim |\gamma_1|^{-3/2}$. But the "equivalent hydrodynamic thickness", e_H, is controlled by the longest loops and should scale like the coil size in solution, R_F. (2) We also extend these considerations to *metastable adsorption*. For instance, starting from the above situation, we assume that the polymer in solution is washed out, leaving an adsorption layer; then the solvent is cooled down to a Θ point: the adsorption layer shrinks significantly. In particular, we predict that all large loops disappear. All results now depend on the sample history: if the layer would have been prepared by contact between a Θ solvent and the wall, we would expect e_H comparable to the Θ solvent coil size. (3) For the repulsive case, the exponents describing the *depletion layer* had been constructed earlier through a tentative argument based on the osmotic pressure near the wall. We rederive these exponents here by a more direct scaling method. For all these cases, we construct the scaling form of the interfacial tension and check the associated Gibbs identities.

I. Introduction

1. Two Regimes. When a solution of neutral, flexible polymer chains is put into contact with a solid wall, two regimes can occur: (a) In many cases the polymer sticks to the wall and cannot be desorbed by washing with the pure solvent.[1] (b) In some cases (in particular with grafted surfaces), the polymer is repelled by the wall, and a depletion layer is expected to build up.[2] Similar effects can take place near the free surface of the solution. Roughly, when the surface tension of the pure polymer melt, γ_p, is lower than the tension of the pure solvent, γ_0, we expect adsorption: this occurs for instance with poly(methylsiloxane) in toluene. On the other hand, if $\gamma_p > \gamma_0$, we expect a depletion layer: this appears to be found with polystyrene in toluene. Detailed measurements on the surface tension of these two systems have been carried out recently.[3]

A copious amount of theoretical work has been carried out on these interfacial systems. The early literature on single-chain adsorption in Θ solvents is reviewed in ref 4. Here, however, we shall be concerned mainly with *good* solvents, where theoretical predictions are more scarce. For simplicity, we shall treat mainly the athermal case, having in mind a Flory–Huggins lattice[5] on which the polymer chains are inscribed: the lattice is cubic with a lattice parameter a and a volume per monomer a^3. Each site can be occupied at most by one monomer; the average occupation or volume fraction is called ϕ. The value of ϕ in the bulk we call ϕ_b.

The mean field theory of the profile $\phi(z)$ (at a distance z from the wall) has been constructed by Jones and Richmond in the attractive case[6] and by Joanny and Leibler in the repulsive case.[2] These mean field theories are analyzed in ref 8 and will not be covered here in more detail because the deviations from mean field are often serious.

Beyond mean field, the *single*-chain adsorption has been clarified by a scaling argument.[7,8] But an early attempt by the present author to discuss the *many*-chain adsorption problem[7a] was a failure: because of a mistake in sign

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in a derivative of the free energy, the regimes found were meaningless.[7b]

2. The Cahn Approach. Stimulated by recent measurements of interfacial tensions,[3] we now return to this question, assuming that a semidilute solution is put in contact with the wall and constructing scaling laws for the concentration profiles. Our discussion is very much related in spirit to the approach of Cahn for the interfacial tension and wetting properties of fluid/solid interfaces.[9] We split the interfacial tension γ into two parts:

$$\gamma = \gamma_d(\phi_s) + I(\phi_s,\phi_b) \tag{I.1}$$

where ϕ_s is the polymer fraction in immediate contact with the wall. More precisely, ϕ_s is defined as the extrapolated value of the concentration profile $\phi(z)$ toward $z = 0$. The actual value of $\phi(z)$ for $z = a$ in the first layer for a lattice model may differ from ϕ_s [$\phi(a) = (l/2)\phi_s$, where l is the average length of "trains" defined by Hoeve]. This length depends on the details of the interactions in the first layer. But all that we need to know about these interactions is contained in the function $\gamma_d(\phi_s)$. The term γ_d describes the interactions in the "proximal" range—i.e., for $z \sim a$. The term $I(\phi_s,\phi_b)$ describes the effects of the concentration profile $\phi(z)$ at larger distances: The deviation of $\phi(z)$ from the bulk value, ϕ_b, costs a certain amount of free energy. A detailed form for I will be discussed later (eq IV.1).

The main assumption hidden in eq I.1 is that the long-range tail ($\sim z^{-3}$) of van der Waals interactions between monomer and wall is not significant. In fact, using the methods of ref 4, one can show that, in mean field, a z^{-3} potential leads to weak (logarithmic) singularities in the profiles. But with the correct scaling theory, the singularity is removed: this is explained in Appendix A.

3. Weak Coupling and Strong Adsorption. We have just seen that it is sufficient to describe the wall–monomer interactions as being of short range, thus allowing the separation of eq I.1 to be significant. The next step amounts to specifying the form of the direct interaction, $\gamma_d(\phi_s)$. In all what follows, we shall reduce this to the simple form

$$\gamma_d = \gamma_0 + \gamma_1\phi_s \tag{I.2}$$

where γ_1 may be positive (=repulsive) or negative (=attractive). With our definition γ_1 has the dimension of energy/cm^2. The essential assumption in eq I.2 is that the monomers *do not fill completely the exposed surface* ($\phi_s \ll 1$). Higher order terms ($\gamma_2\phi_s^2$, ...) would describe interactions between monomers in the first layer. The condition $\phi_s \ll 1$ will be easily satisfied in the repulsive case ($\gamma_1 > 0$), where ϕ is much smaller than the bulk value, ϕ_b, and the latter is itself small for a semidilute solution. But if γ_1 is negative, we have to be more careful: to ensure $\phi_s < 1$, we shall require that

$$\gamma_1 < kTa^{-2}$$

This defines what may be called a weak-coupling limit.

It is important to realize that this limit *remains compatible with strong adsorption.* This can be understood on the single-chain problem, following ref 7 and 8. An adsorbed chain (with N monomers) has a finite fraction f of its monomers which are in direct contact with the wall: the reversible work required to suppress these bonds is $fN\gamma_1a^2$, and the partition coefficient of the chains between bulk and adsorbed is proportional to

$$p = \exp\left(-k_0 fN\frac{|\gamma_1|a^2}{kT}\right) \tag{I.3}$$

where k_0 is a numerical constant. (There is also an entropy increase when the chain desorbs, and the resulting contribution to the free energy is the source of the modified coefficient k_0 in eq I.3.) Weak coupling means that γ_1a^2/kT is small; but, because of the factor N, this is still compatible with huge values of the exponent in eq I.3, giving a very strong adsorption. Note, incidentally, that the self-consistent discussion of ref 7 and 8 gives us the scaling structure of $\mathcal{F}$. For clarity, we repeat the argument below. We assume that our chain has loops extending on a thickness D from the wall.

In quantitative terms, this means that the concentration profile has the scaling structure

$$\phi(z) = \phi_s g(z/D) \qquad (z \gg a)$$

where $g(x) \to 0$ when $x \gg 1$. The number of monomers in contact with the wall (per unit area) is proportional to ϕ_s/a^2. The proportionality constant is $l/2$ (l = "average train size" of Hoeve). The total number of monomers per unit area is

$$\Gamma = \int \phi(z)a^{-3}\,dz$$

The fraction at the wall is thus

$$f = (\text{const})\phi_s a^{-2}/\Gamma = (\text{const})a/D$$

The free energy per chain, $\mathcal{F}_c$, contains two D-dependent terms:

$$(kT)^{-1}\mathcal{F}_c = \left(\frac{R_F}{D}\right)^{5/3} - |\gamma_1|a^2\frac{a}{D}N \tag{I.4}$$

The first term is the confinement energy and $R_F = N^{3/5}a$ is the Flory radius of a chain in the bulk solvent. The second term is the free energy associated with contact points. All numerical factors are omitted. Minimization of (I.4) gives a result which is independent of N:

$$f = \frac{a}{D} \cong \left(\frac{|\gamma_1|a^2}{kT}\right)^{3/2} \tag{I.5}$$

We shall see that this relation $D(\gamma_1)$ retains a meaning for all interfacial problems in good solvents; it defines one fundamental length D associated with the concentration profiles (both for positive and negative γ_1).

4. Limits of Validity of the Calculation. We shall constantly assume that D satisfies simultaneously two inequalities:

$$a \ll D \ll \xi_b \tag{I.6}$$

The first inequality is just a restatement of the weak-coupling limit. The interest of this limit lies in the fact that, for $D \gg a$, the answers become independent of the details of the model. (Conversely, if we put $D \sim a$ the detailed atomic arrangements, and the exact form of the short-range forces, would become relevant.) The second inequality of (I.6) involves the correlation length of the polymer solution, ξ_b (where b stands for bulk). The structure and meaning of ξ_b have been discussed extensively;[8,10] for our purposes, the following properties should be kept in mind:

(a) ξ_b is a decreasing function of ϕ_b:

$$\xi_b = a\phi_b^{-3/4} \tag{I.7}$$

(b) The osmotic pressure of the solution, Π, scales as[11]

$$\Pi \sim kT\xi_b^{-3} \sim kTa^{-3}\phi^{2.25} \tag{I.8}$$

(c) The chemical potential of one monomer in the solution is

$$\mu \sim \Pi a^3/\phi_b \sim kT\phi_b^{5/4} \tag{I.9}$$

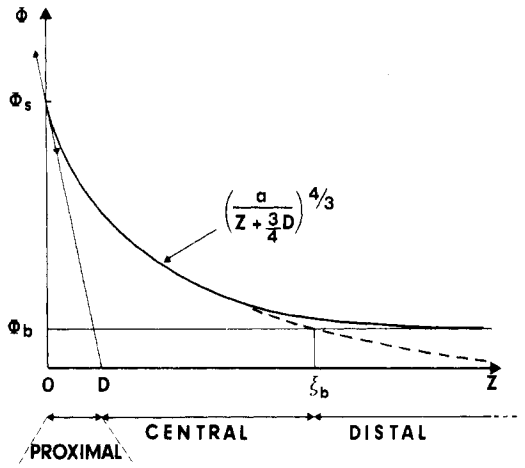

Figure 1. Qualitative plot of the polymer volume fraction (ϕ) vs. distance (z) from an adsorbing wall. The extrapolation length D is fixed by the "free energy of sticking", γ_1, of monomers on the wall. Full line: profile $\phi(z)$ for a finite volume fraction ϕ_b in the bulk solution. Dotted line: profile extrapolated to $\phi_b = 0$. The two profiles coincide up to a distance ξ_b (the correlation length in the bulk solution).

Since we are dealing with *semidilute* solutions (overlapping chains), we must have

$$\phi_b > \phi^* = N^{-4/5} \tag{I.10}$$

Setting $\phi_b = \phi^*$ corresponds to $\xi_b = R_F$. This remark has one important consequence for the attractive case: we can let $\phi_b \to 0$ and *still obtain a significant profile* $\phi(z)$, provided that we use it for distances $z < R_F$ (where R_F is the natural size of a single coil in solution). Thus, the present paper may be applicable to certain properties of adsorbed polymer films *in the presence of pure solvent*: ellipsometry, surface excess, etc., which are mainly controlled by the region $z \sim D$. On the other hand, other properties which are sensitive to the biggest loops (of size R_F) cannot be predicted in detail: this occurs, for instance, if we investigate the modification of flow boundary conditions induced by the existence of an adsorbed layer (Appendix B).

5. Three Regions in Space. The concentration profiles are shown qualitatively on Figure 1 for the attractive case and on Figure 2 for the repulsive case. There are three distinct regions in each figure.

(a) Proximal ($z \sim a < D$). Here the effects of the short-range forces between a monomer and the wall are important.

(b) Central ($D < z < \xi_b$). Here the profile is strongly universal and becomes independent of the bulk concentration ϕ_b.

(c) Distal ($z > \xi_b$). Here the concentration relaxes exponentially toward the bulk value:

$$\frac{\phi(z) - \phi_b}{\phi_b} \sim \exp(-z/\xi_b) \tag{I.11}$$

Our main concern here will be with the central domain. Our precise definition of the length D will be by an extrapolation of the slope of the central profile toward $z \to 0$. We write

$$\left|\frac{1}{\phi}\frac{d\phi}{dz}\right|_{\text{central } z\to 0} = \frac{1}{D} \tag{I.12}$$

(The derivative $d\phi/dz|_0$ is negative for adsorption, but we find it convenient to define D as positive in all cases.)

There is an important difference between the boundary condition (I.12) and what is found in the Cahn approach for simple fluids: in the latter case, what is fixed by γ_1 is the slope $d\phi/dz|_0$. But in the polymer case, γ_1 is related to a *logarithmic derivative* $\phi^{-1}(d\phi/dz)|_0$. To understand this, it is helpful to return first to the mean field discussion of ref 4 and 8. In the mean field approach, the essential object is an order parameter $\psi(z)$ such that $\phi(z) \equiv |\psi(z)|^2$. The energy functional has a simple structure when expressed in terms of ψ (not of ϕ) and is

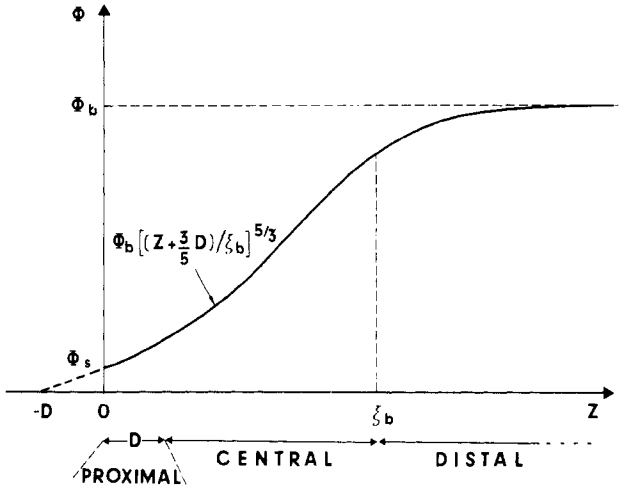

Figure 2. Qualitative profile $\phi(z)$ for a *repulsive* wall. Note that in this case, the profile is *not* independent of the bulk concentration, ϕ_b, in the central region.

$$\gamma - \gamma_0 = \gamma_1|\psi_s|^2 + \int_0^\infty \left[\frac{1}{2}L\left(\frac{d\psi}{dz}\right)^2 + G(\psi^2)\right] dz \tag{I.13}$$

where L is constant and G is an interaction term, which we need not specify here. Minimizing this with respect to ψ_s gives

$$2\gamma_1\psi_s - L\left.\frac{d\psi}{dz}\right|_0 = 0$$

and it is indeed a logarithmic slope which matters. We have

$$\frac{1}{\phi}\frac{d\phi}{dz}\bigg|_0 = \frac{2}{\psi}\frac{d\psi}{dz}\bigg|_0 = \frac{2\gamma_1}{L} = \frac{1}{D}\bigg|_{\text{mean field}} \tag{I.14}$$

(In ref 4 and 8, we use a different notation and put $\kappa = (1/\psi)\, d\psi/dz|_0 = 1/2D_{mf}$.) Thus, in mean field, the extrapolation length, D_{mf}, is inversely proportional to the free energy of sticking.[20] With a correct scaling theory, the problem of boundary conditions is more complex. We can always *define* a length D by eq I.12. But one of our tasks will be to calculate D by scaling arguments. For good solvents the (remarkably simple) result, to be shown later, is that D coincides with the length introduced in eq I.5: this holds for repulsive, and also for attractive, walls.

We now have collected all our assumptions and definitions. Our aim is to start with a given sticking energy, γ_1, and to predict from it the concentration profile in the central region. Some scaling results have already been published[7,8] but they dealt only with cases of strong coupling ($D \sim a$), and mainly with the repulsive case. Here, we insist much more on the description of adsorption and show in particular that the adsorbed polymer layer must have a very remarkable self-similar structure (Figure 3).

II. Polymer Adsorption

1. Profile in the Central Region ($D \ll z \ll \xi_b$). As is clear from Figure 1, we are dealing here with concen-

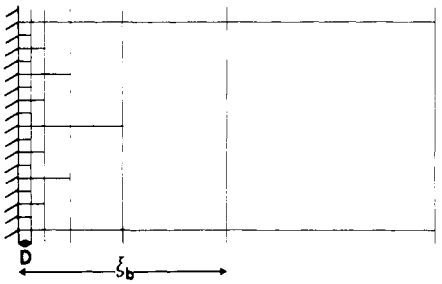

Figure 3. Pictorial representation of the self-similar solution for the concentration profile in *adsorption*. At distances $z > \xi_b$ from the wall, the solution can be pictured as a transient, random network of mesh ξ_b: to simplify the drawing, this is represented as a square mesh. For $z < \xi_b$, the mesh size gets smaller, but at any z in this range, the mesh size is of order z. The process stops at a minimal $z = D$ dependent on the strength of the wall attraction $|\gamma_1|$.

trations $\phi \gg \phi_b$, and thus we may let $\phi_b \to 0$ in our discussion. In this situation, it is very useful to define a local correlation length $\xi(\phi)$ associated with the local concentration ϕ. Since no other length is available (for $\phi \gg \phi_b$), we must define $\xi(\phi)$ by a generalization of eq I.7, namely

$$\xi(\phi) = a\phi^{-3/4} \tag{II.1}$$

If we know the profile $\phi(z)$ and stand at a given distance z from the wall, we can construct a value of $\xi[\phi(z)]$: thus we have defined a function $\xi(z)$. But, since no other length enters in the problem, the only possible function $\xi(z)$ is $\xi = (\text{const})z$. Thus the profile is defined by

$$\xi[\phi(z)] \cong z \tag{II.2}$$

$$\phi = (a/z)^{4/3} \qquad (D \ll z \ll \xi_b) \tag{II.3}$$

Equation II.2 is typical of a *self-similar structure* and is qualitatively illustrated on Figure 3. The "mesh size" of the polymer solution decreases near the wall, always remaining comparable to the distance z itself.

2. Boundary Conditions and Free Energy Balance. To incorporate the boundary condition (I.12) into the profile, we modify eq II.3 to

$$\phi(z) \cong \left(\frac{a}{z + \frac{4}{3}D}\right)^{4/3} \tag{II.4}$$

The concentration drops by a factor of order 2 in a thickness of order D; for many properties, D is the effective thickness of the adsorbed layer. Note that

$$\phi_s \equiv \phi(z = 0) \cong (a/D)^{4/3} \tag{II.5}$$

We shall now determine ϕ_s and $D \cong \xi(\phi_s)$ by a suitable minimization of the Cahn free energy (eq I.1). Our first task is to construct the internal contribution $I(\phi_b,\phi_s)$. For the attractive case ($\phi_s \gg \phi_b$), we can assume (and check later) that I depends only on the dominant concentration ϕ_s. We derive $I(\phi_s)$ as follows. In a polymer solution of concentration ϕ, the local energy density is $kT/\xi^3(\phi)$ (as indicated by eq I.8) and this has to be integrated over a thickness $\sim D \sim \xi(\phi_s)$. Thus

$$I(\phi_s) \cong \frac{kT}{D^2} \cong \frac{kT}{a^2}\phi_s^{3/2} \tag{II.6}$$

We can, now, minimize the interfacial energy γ (eq I.1) with respect to ϕ_s or D. Choosing D as our variable

$$\gamma - \gamma_0 \cong -|\gamma_1|\left(\frac{a}{D}\right)^{4/3} + \frac{kT}{D^2} \tag{II.7}$$

and the optimum D reproduces eq I.5 exactly, as announced earlier. At the optimum D, the two terms are comparable and we have

$$\gamma - \gamma_0 \cong -kT/D^2 = -\frac{kT}{a^2}\left(\frac{\gamma_1 a^2}{kT}\right)^3 \tag{II.8}$$

Equation II.8 is the result for $\phi_b/\phi_s \ll 1$ (or $D \ll \xi_b$). It describes the interfacial energy of an adsorbed film in equilibrium with nearly pure solvent. Let us now discuss the surface excess Γ:

$$\Gamma = \int_0^\infty a^{-3}\phi(z)\, dz \cong a^{-2}(a/D)^{1/3} \tag{II.9}$$

Note that Γ is related to the surface concentration $\phi_s a^{-2}$ by $\Gamma f = \phi_s a^{-2}$, where $f \cong a/D$, just as in eq I.4 and I.5. An important worry must be mentioned at this point: our prediction is that Γ be independent of molecular weight (for long chains). For layer thicknesses much smaller than an optical wavelength, we would expect that the ellipsometric data essentially measure Γ. But the results of ref 12 give an ellipsometric thickness *increasing with molecular weight*: we have no explanation for this discrepancy.[21]

Let us now analyze the concentration dependence of the interfacial tension. Since our Γ is (to a first approximation) independent of ϕ_b, the Gibbs equation $d\gamma/d\mu = -\Gamma$ can be integrated directly to give

$$\gamma - \gamma_0 = -\frac{kT}{D^2} - \Gamma\mu \tag{II.10}$$

and inserting the scaling form (I.9) for μ, we reach

$$\gamma - \gamma_0 = -k_1\frac{kT}{D^2}\left[1 + k_2\left(\frac{D}{\xi_b}\right)^{5/3}\right] \qquad (D < \xi_b) \tag{II.11}$$

where k_1 and k_2 are unknown numerical constants. The concentration-dependent term varies like $\phi_b^{5/4}$. There are but few data which can be meaningfully compared with (II.11). But the general trends observed on PDMS/toluene free surfaces do agree with (II.11).[3]

3. Changing the Environment of an Adsorbed Layer. Let us perform the following sequence of operations: (a) We put the wall into contact with the polymer solution in good-solvent conditions: the profile (II.3) builds up. (b) We wash out the solution with pure solvent. As explained after eq I.10, we expect to retain an adsorption layer with the same profile up to a large distance $z \sim R_F$. (Appendix B shows that the equivalent hydrodynamic thickness e_H of the layer is then of order R_F.) (c) We now cool down the solvent and bring it to the Flory Θ temperature, where the pairwise effective monomer–monomer interaction vanishes.[5] What happens to the profile and to e_H?

A plausible answer to this question can be obtained from mean field theory, this approach being acceptable in Θ conditions. We then deal with an order parameter $\psi(z)$ such that $|\psi(z)|^2$ gives the local number density, $\rho(z)$. The free energy per unit area of wall has the structure[8]

$$\gamma = \gamma_d(\rho_s) + kT\int dz\left[\frac{a^2}{6}\left(\frac{d\psi}{dz}\right)^2 + \frac{w^2}{6}|\psi|^6\right] \tag{II.12}$$

where w has the dimensions (and the order of magnitude) of a monomer volume. Note that there is no ψ^4 term for $T = \Theta$.

We *assume* that the layer reaches an equilibrium (i.e., minimizes γ), but with one constraint: the overall surface coverage Γ must be kept constant (no chain is desorbed during stage c). For our case, Γ is fixed by eq II.9.

Technically, this leads us to write the following variational condition:

$$\delta\gamma = \mu\delta\Gamma = \mu\delta\int|\psi|^2\,dz \qquad \text{(II.13)}$$

But the Lagrange multiplier μ is not an equilibrium chemical potential. At the end of the calculation, μ is obtained by imposing the value (II.9) for Γ. It will turn out that μ is negative and conveniently expressed in terms of a density parameter ρ_0 as follows:

$$\mu = -\tfrac{1}{6}(w\rho_0)^2kT \qquad \text{(II.14)}$$

Then, writing down the explicit variational eq II.13 and taking the first integral, we arrive at

$$\frac{a^2}{6}\left(\frac{d\psi}{dz}\right)^2 = \frac{w^2}{6}\psi^2(\psi^4 + \psi_0^4) \qquad \text{(II.15)}$$

The profile $\rho(z)$ is then given by the implicit equation

$$\frac{2wz}{a} = \int_{\rho(z)}^{\rho_s}\frac{d\rho}{\rho}\,(\rho_0^2 + \rho^2)^{-1/2} \qquad \text{(II.16)}$$

where ρ_s is the density at the wall. Using the extrapolation length D, and eq II.15, we have a further equation for ρ_s:

$$\frac{1}{D_{mf}} = -\frac{2}{\psi}\frac{d\psi}{dz}\bigg|_0 = \frac{2w}{a}(\rho_0^2 + \rho_s^2)^{1/2} \qquad \text{(II.17)}$$

where D_{mf} is defined by eq I.14 in terms of Γ_1. The surface excess Γ is given by

$$\Gamma = \int_0^\infty \rho\,dz = \int\rho\frac{dz}{d\psi}\,d\psi$$
$$= \int_{\rho(z)}^{\rho_s} d\rho\,(\rho_0^2 + \rho^2)^{-1/2} \qquad \text{(II.18)}$$

Putting $\rho = \rho_0 \sinh t$ the integrals can be performed, and the results are

$$\rho_0 = \frac{a}{2wD_{mf}}\left[\cosh\left(\frac{2w\Gamma}{a}\right)\right]^{-1}$$
$$\rho_s = \frac{a}{2wD_{mf}}\tanh\left(\frac{2w\Gamma}{a}\right) \qquad \text{(II.19)}$$

In these formulas, we must insert the value (II.9) for Γ. Taking $w \sim a^3$, this leads to

$$2w\Gamma/a \sim (a/D)^{1/3} \qquad \text{(II.20)}$$

This parameter is smaller than unity in the weak-coupling limit. Thus (returning to II.19), we have

$$\rho_0 \cong a/2wD_{mf} \qquad \text{(II.21)}$$

Having expressed all the relevant quantities in terms of Γ, we can now return to the profile (eq II.16). At short distances ($\rho > \rho_0$)

$$\rho(z) = a/2w(z + D_{mf}) \qquad \text{(II.22)}$$

At longer distances ($\rho \ll \rho_0$), we have

$$\frac{2wz}{a} \to \frac{1}{\rho_0}\int_{\rho(z)}^{\rho_0}\frac{d\rho}{\rho} + \text{const} \cong \frac{1}{\rho_0}\ln\frac{\rho_0}{\rho(z)}$$

$$\rho(z) = (\text{const})\exp\left(-z\frac{2w\rho_0}{a}\right)$$
$$\sim \exp(-z/D_{mf}) \qquad (z > D_{mf}) \qquad \text{(II.23)}$$

Equation II.23 is the central result of this discussion: it shows that the transfer from good-solvent conditions to Θ solvent should *strongly reduce the hydrodynamic thickness* of the adsorbed layer. We now expect

$$e_H \sim D_{mf} \ll R_F \qquad \text{(II.24)}$$

It is important to realize that this result holds only if the preparation of the layer has followed the three stages a, b, and c described above. If we followed a different path to reach the same final conditions, we would expect a different e_H. For instance, if we put the wall in contact with the solution at $T = \Theta$ and then wash out the solvent, we expect to retain all chains which are within a radius $R_0 \sim N^{1/2}a$ of the wall. For $z < R_0$ the profile is then given by (II.22). The hydrodynamic thickness e_H for the preparation is then seen (by the methods of Appendix B) to be of order R_0—i.e., enormously larger than (II.24). This type of dependence has indeed been observed for adsorbed layers (on glass) of polystyrene in *trans*-decahydronaphthalene (at the Θ point).[19]

To summarize: our discussion of adsorbed layers can be extended to situations where we do *not* have equilibrium with the ambient solution. Because of the large sticking energy per chain, we treat these situations assuming that the coverage Γ is constant and minimizing a free energy with this constraint added. Of course, we do not know whether this constrained equilibrium can be reached in a reasonable time scale: reptation in partly adsorbed chains is an extremely complex phenomenon.

III. The Repulsive Case

Here we return to Figure 2 and start with the central domain; the depletion layer may be described by the scaling form

$$\phi(z) = \phi_b f(z/\xi_b)$$
$$\to \phi_b(z/\xi_b)^m \qquad (D < z < \xi_b) \qquad \text{(III.1)}$$

where the exponent m is to be determined. If we extend this to the proximal region, to satisfy boundary condition I.12, we must put

$$\phi(z) = \phi_b\left(\frac{z + mD}{\xi_b}\right)^m \qquad a < z < \xi_b \qquad \text{(III.2)}$$

Since $D \ll \xi_b$, $\phi(z)$ is much smaller than the bulk value ϕ_b at all distances z satisfying the inequality $z < \xi_b - mD$. This defines the thickness e of the depletion layer. Ignoring coefficients

$$e \cong \xi_b - D \qquad \text{(to first order in } D/\xi_b) \qquad \text{(III.3)}$$

The value of the concentration on the surface layer is

$$\phi_s \cong \phi_b(D/\xi_b)^m \qquad \text{(III.4)}$$

We can now construct the Cahn interfacial energy γ and derive m by minimization of γ. Our starting point is

$$\gamma - \gamma_0 = \gamma_1\phi_s + \Pi e \qquad \text{(III.5)}$$

The last term (Πe) represents the work done against the osmotic pressure, Π, to remove the solute from a depletion layer of thickness e. Thus using (I.8) and (III.4), we get

$$\gamma - \gamma_0 = \gamma_1\left(\frac{a}{\xi_b}\right)^{4/3}\left(\frac{D}{\xi_b}\right)^m + \frac{kT}{\xi_b^2} - \frac{kTD}{\xi_b^3} \qquad \text{(III.6)}$$

where we have chosen as variables the lengths D and ξ_b rather than the concentrations ϕ_s and ϕ_b. We can now minimize (III.6) with respect to D, obtaining

$$\frac{\gamma_1 a^2}{kT} = \xi_b^{m-5/3}a^{2/3}D^{1-m} \qquad \text{(III.7)}$$

This must be satisfied for all ϕ_b (all ξ_b): thus we must put $m = {}^5/_3$. This result was already conjectured,[7,8] but the present derivation is much more transparent. Secondly, inserting $m = {}^5/_3$ in eq III.7, we find that, once more, the relation between the sticking energy, γ_1, and the extrapolation length, D, retains the form (I.5).

After minimization, the interfacial energy has the scaling structure

$$\gamma - \gamma_0 \cong \frac{kT}{\xi_b^2} - \frac{kTD}{\xi_b^3} \qquad (D \ll \xi_b) \qquad \text{(III.8)}$$

The leading term is kT/ξ_b^2 and from eq I.7 it is proportional to $\phi_b^{3/2}$. Recent data by Ober on the free surface of polystyrene + toluene solutions[3] seem to show that type of behavior in the semidilute regimes ($\phi_b \ll 1$).

Note finally that the Gibbs identity is correctly satisfied by the scaling form (III.8). The surface excess Γ is negative

$$\Gamma \cong -\phi_b a^{-3} e \cong -\phi_b a^{-3}(\xi_b - D)$$

and from the form (I.9) of the chemical potential μ, we can check that $d\gamma/d\mu = -\Gamma$.

IV. Conclusions

1. It is possible to generate a consistent scaling picture for a polymer solution near a wall, assuming that a true equilibrium is realized. Of course, in the attractive case, with a solid wall, equilibrium may be hard to achieve; the reptation of chains which are partly attached may be strongly hindered. But for chains near a fluid/fluid interface, this difficulty is hopefully not too serious.

2. The scaling picture predicts a structure for the adsorption layer which is nearly independent of the bulk concentration, self-similar, and rather strongly universal, provided that $D \gg a$, i.e., that the free energy of sticking is not too large. Unfortunately, conventional ellipsometric experiments[12] are mainly sensitive to the overall surface excess and not very dependent on the detailed shape of the concentration profile. On the other hand, the hydrodynamic barrier thickness[13] (measured through the mobility of a solid particle coated with polymer) is more sensitive to the outer layer ($z \sim R_F$ for dilute solutions) than to the central region ($D < z < R_F$): this is explained in Appendix B.

3. For the repulsive case, a study of the depletion layer by optical evanescent waves has recently been started in our group, but the major laws (thickness proportional to $\phi_b^{-3/4}$) have not yet been proven experimentally.

4. From a physicochemical point of view, the most interesting aim is to vary systematically the free energy of sticking, γ_1, and in particular to cross over from positive to negative values of γ_1. This is probably within reach, if the solid surface is coated by a variable amount of (short) grafted molecules.

5. A computational point: some readers may suffer from the lack of precise formulas which occurs in a pure scaling analysis of the present type. It may be possible to improve on this by a method which we call the *Widom approach*: to determine the density profile $\rho(x)$ at a liquid/gas interface, Widom noticed that a free energy functional containing the correct critical exponents for the homogeneous system ($d\rho/dx = 0$) plus a term ${}^1/_2 L(d\rho/dx)^2$, where L is independent of ρ, reproduces rather well the scaling structure of the interface.[14] In the present case, we may try something similar. There is a difference however: L is a function of concentration even in mean field.[15] But our essential assumption is that terms of order $(\nabla\phi)^2$ are sufficient to describe the situation. If we do this, we come out with the following functional form:

$$\frac{\gamma - \gamma_d}{kT} = \int \frac{dz}{a^3}\left[\frac{C_1}{\phi^x(\phi_b + \phi)^y}\left(\frac{d\phi}{dz}\right)^2 + C_2\phi^{\nu d/(\nu d-1)} - \frac{\mu}{kT}\phi + \frac{a^3}{kT}\Pi(\phi_b)\right] \qquad \text{(IV.1)}$$

where C_1 and C_2 are two numerical constants and x and y are two exponents, which we write below in their most general form:

$$x = 2(1 - \nu) \qquad \text{(IV.2)}$$

$$y = \frac{\nu d(2\nu - 1)}{\nu d - 1} \qquad \text{(IV.3)}$$

Here d is the dimensionality ($d = 3$ in practice) and ν is the "excluded volume exponent" associated with the radius of gyration of a single coil ($R_F \cong aN^\nu$): $\nu \sim {}^3/_5$ in three dimensions and thus

$$x \cong {}^4/_5$$

$$y \cong {}^9/_{20} \qquad \text{(IV.4)}$$

Starting from the functional (IV.1) with the exponents (IV.4), one can rederive all the scaling results of the present paper. But the functional allows one to do more: (a) one could find detailed profiles $\phi(z)$ for both cases, even in the transition region $z \sim \xi_b$. (b) For more complicated geometries (e.g., colloidal grains of size comparable to D) one could predict the profiles and the intergrain interactions.

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Appendix A. Effects of Long-Range van der Waals Attractions

Let us consider a wall attracting each monomer by a long-range potential of the form

$$U(z) = -H(a/z)^3 \qquad \text{(A.1)}$$

where H has the dimension of our energy and is usually of order 100 K $\sim 10^{-2}$ eV or less. (Note that U is the *difference* in attraction potentials between the monomer and an equal volume (a^3) of solvent.)

Our aim is to find out whether the potential (A.1) can alter the self-similar concentration profile (II.3) up to large distances. The starting point, in the Widom approach of section IV, will be to write a free energy functional of the form

$$\mathcal{F} = \int_0^\infty dz \left\{\frac{kT}{\xi^3(\phi)}\left[1 + \left(\frac{\xi(\phi)\, d\phi}{\phi\, dz}\right)^2\right] - \frac{H\phi}{z^3}\right\} \qquad \text{(A.2)}$$

Equation A.2 can be checked to be equivalent to (IV.1) in the limit $\phi \gg \phi_b$, with the addition of the external potential U. It is convenient to change variables and to set

$$\psi = \phi^{3/8} \qquad \text{(A.3)}$$

leading to a simple structure for the gradient terms: $(d\psi/dx)^2 \times$ (const) and to an equilibrium equation of the form

$$-a^2\frac{d^2\psi}{dz^2} + \psi^5 - \alpha\left(\frac{a}{z}\right)^3\psi^{5/3} = 0 \qquad \text{(A.4)}$$

where $\alpha = H/kT$ and where all numerical constants are again omitted. A further change in scales is useful. Putting

$$z = \alpha^{3/4}ax$$
$$\psi = \alpha^{3/8}u \tag{A.5}$$

we arrive at

$$-\frac{d^2u}{dx^2} + u^5 - \frac{1}{x^3}u^{5/3} = 0 \tag{A.6}$$

The boundary condition at the wall has to be defined. A simple case corresponds to the assumption that we have a hard wall and no special attractive force at short distances. Then we simply set $\phi(z = 0) = 0$ or $u(x = 0) = 0$. The solution of (A.6) is then relatively simple:
(a) *At short distances* ($x < 1$) u is an increasing function of x:

$$u = (\text{const})x^{3/2} \tag{A.7}$$

In this regime, the u^5 term is negligible in eq A.6.
(b) *At longer distances* ($x > 1$) the $u^{5/3}$ term of (A.6) becomes negligible, and we have a profile

$$u = (\text{const})x^{-1/2} \qquad (x \gg 1) \tag{A.8}$$

This is the self-similar solution of eq II.3. An improved solution at large x is

$$u = (\text{const})(x + x_0)^{-1/2} \tag{A.9}$$

Since x_0 is defined though a purely dimensionless equation (eq A.6), it is just a number. On the other hand, x_0 is related to the extrapolation length D by the following condition acting on (A.9):

$$\left.\frac{d\phi}{\phi\, dz}\right|_{z\to 0} = \frac{8}{3}\left.\frac{du}{u\, dz}\right|_{z\to 0} = -\frac{1}{D}$$

Using eq A.5, this gives

$$D = \tfrac{4}{3}x_0\alpha^{3/4}a = (\text{const})\alpha^{3/4}a \tag{A.10}$$

We conclude that, even for very strong, long-range, van der Waals potentials, the self-similar solution (A.8) is perturbed only in a region $\alpha^{3/4}a$. Our analysis, assuming continuous variations, etc., is meaningful only for $\alpha^{3/4}a > 1$ or $\alpha > 1$. In practice, we expect α to be smaller ($\alpha \lesssim 1$): it is then clear that is no special long-range effect is expected.

Appendix B. Effective Hydrodynamic Thickness of the Adsorbed Layer

We consider here a weak shear flow

$$v_x = v(z)$$
$$v_y = v_z = 0$$

near the adsorbing wall in the limit $\phi_b \to 0$ (flows of the pure solvent). At long distances from the wall, assuming no pressure head along z, the stress σ_{xz} imposes a constant slope:

$$\eta_s \frac{dv(z)}{dz} = \sigma_{xz} = \text{const} \tag{B.1}$$

(where η_s is the solvent viscosity). Thus

$$v(z) = \frac{\sigma_{xz}}{\eta_s}(z - e_H) \tag{B.2}$$

where e_H is the effective hydrodynamic thickness of the adsorbed layer. To determine e_H, one must find the profile $v(z)$ *inside* the adsorbed layer. A general discussion of these profiles has been given by Silberberg,[16] who pointed out an analogy between the adsorbed layer and a gel. Detailed calculations of $v(z)$ for exponential concentration profiles have been carried out in Strasbourg.[13] Here we shall construct $v(z)$ using dynamical scaling arguments.[17] The starting point is a local force balance of the form

$$\eta_s\frac{d^2v}{dz^2} - \zeta(z)v \tag{B.3}$$

where $\zeta(z)$ is the friction coefficient between solvent and polymer at point z. The standard assumption would be to take $\zeta(z)$ proportional to the local concentration $\phi(z)$. This, however, is not correct! We must think of the structure in terms of a porous medium, with mesh size $\xi(\phi)$. For such a medium, the friction coefficient entering in Darcy's law is known to scale like[18]

$$\zeta \cong \eta_s/\xi^2(\phi) \tag{B.4}$$

Note that this form of friction gives $\zeta \sim \phi^{3/2}$ rather than $\zeta \sim \phi$. For our present purposes, from eq II.2, we know that $\xi(\phi) = z$ in the central region. Thus we predict

$$\zeta = Q\eta_s/z^2 \qquad (Q > 0) \tag{B.5}$$

The numerical constant Q is unknown but plays an important role in the hydrodynamic problem: inserting (B.5) into (B.3), we see immediately that the solution which vanishes at $z = 0$ is

$$v(z) = (\text{const})z^l \tag{B.6}$$

where $l(l + 1) = Q$. This solution will hold up to the maximum allowed distance $z \sim R_F$ (as explained after eq I.10). At longer distances eq B.2 holds. We can thus write

$$\left.\frac{1}{v}\frac{dv}{dz}\right|_{z=R_F} = \frac{l}{R_F} \tag{B.7}$$

and comparing this with (B.2), we arrive at

$$e_H = R_F(1 - 1/l)$$

Thus, e_H *scales like* R_F: the hydrodynamic effects are dominated by the largest loops, as stated in section II.

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(20) To make contact with the classical literature in this field, it is instructive to write down the full equation of $\psi(z)$ obtained by minimization of eq I.13. Consider, for instance, the noninteracting case where G reduces to a classical potential term $(-\mu\psi^2)$. Then ψ (and the concentration ψ_2) has the exponential form discussed by Hoeve, Rubin, and others: see ref 4 for a review of these aspects.
(21) It has been pointed out to us by E. A. DiMarzio that if the surface is heterogeneous and has only a few spots of strong attraction (possibly related to steps or dislocations on the solid), one expects that Γ does increase with M.

Miscibility of the Poly(hydroxy ether) of Bisphenol A with Water-Soluble Polyethers

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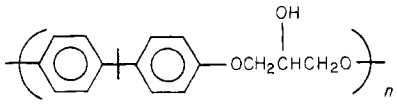
ABSTRACT: The miscibility of the poly(hydroxy ether) of bisphenol A (phenoxy) with the water-soluble polyethers poly(ethylene oxide) and poly(vinyl methyl ether) has been established by using dynamic mechanical methods. The observed miscibility is proposed to be the result of specific interactions between the pendant hydroxyl of phenoxy (proton donor) and the ether group of the respective polyethers (proton acceptor). Poly(propylene oxide) and poly(vinyl ethyl ether) are both water insoluble and do not exhibit miscibility with phenoxy, presumably due to poorer hydrogen-bonding capabilities for these polyethers (as evidenced by the water insolubility). The addition of phenoxy to poly(ethylene oxide) significantly lowers the crystallization rate, as expected, due to a T_g increase. This allows the preparation of amorphous specimens and, thus, the extrapolation of T_g–composition data to determine the T_g of amorphous poly(ethylene oxide) (–73 °C). A significant T_g increase occurs with the crystallization of poly(ethylene oxide) from blends with phenoxy due to an increase in the amorphous phase concentration of phenoxy and chain stiffening due to the presence of spherulitic structure. From the T_g shift and a simple material balance, the degree of crystallinity and $\Delta H_f°$ of poly(ethylene oxide) can be directly calculated. These data were used to calculate a degree of crystallinity of 70% for the unblended poly(ethylene oxide), in excellent agreement with previously reported data obtained by more classical techniques.

Introduction

In the past decade, many examples of miscible polymer pairs have been cited in the technical literature,[1] indicating that preparation of miscible polymer systems was more feasible than previously believed.[2] Many of the recently reported miscible systems are believed to achieve miscibility via specific interactions (e.g., hydrogen bonding). Phenoxy, the poly(hydroxy ether) of bisphenol A, offers



phenoxy

excellent potential for hydrogen bonding as a proton donor because of its pendant hydroxyl. Phenoxy has been previously shown to exhibit miscibility with poly(ε-caprolactone),[3] poly(butylene terephthalate),[4] a cyclohexanedimethanol-based polyester,[4] a polyester-based polyurethane,[5] poly(ethylene adipate),[6] and poly(butylene adipate).

Poly(ethylene oxide), a water-soluble polymer, exhibits miscibility with poly(acrylic acid),[7] poly(methacrylic acid),[8] a vinyl methyl ether/maleic anhydride copolymer,[9] (carboxymethyl)cellulose sodium salt,[9] and (carboxymethyl)dextran.[9] These miscible blends exhibit particularly strong specific interactions and thus are generally referred to as complexes. Although the above-mentioned poly(ethylene oxide) blends are with other water-soluble polymers, at neutral or low pH a precipitate is immediately formed when water solutions of the respective constituents are mixed. Other samples of complexation involving poly(ethylene oxide) include blends with polyureas and phenolics.[9] Poly(ethylene oxide) acts as the proton acceptor in the hydrogen-bonding interactions with these polymers.

With this background, phenoxy/poly(ethylene oxide) blends have an excellent potential for hydrogen-bonding interactions and therefore the phase behavior of their blends would be expected to be quite interesting. Indeed this is the case, and miscibility over the entire composition range was observed and is the subject of this paper.

Another water-soluble polyether, poly(vinyl methyl ether) (PVME), is expected to interact as a proton acceptor in blends with proton-donor polymers. Blends of PVME with phenoxy are also miscible over the entire composition range, as will be illustrated by the data reported in this paper. PVME/polystyrene blends have been reported as miscible in various investigations[10–12] and are particularly studied in regard to the observed lower critical solution temperature (LCST) behavior.[10,11,13] Phenoxy/PVME blends interestingly also exhibit LCST behavior. Lower critical solution temperature behavior, in which phase separation occurs with increasing temperature, is typical for mixtures of high molecular weight polymers.

Experimental Section

Blends of phenoxy (PKHH, Union Carbide Corp.; reduced viscosity = 0.43 dL/g measured as 0.2 g/100 mL in tetrahydrofuran at 25 °C) and poly(ethylene oxide) (WSR-301, Union Carbide Corp.; molecular weight approximately 4 000 000) were prepared in a brabender at 175–190 °C for 8–10 min. The resultant mixtures were then compression molded into 30-mil thick samples at 160–180 °C. Except where specifically designated, the samples were stored in a vacuum desiccator until testing. Dynamic mechanical measurements were made with a torsion pendulum

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