Swelling of Macromolecules Grafted on Inert Surfaces and Partitioning of a Solute between Solvent and Grafted Phase

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ABSTRACT: A method is proposed for determining the thermodynamic characteristics of macromolecules grafted on an inert plane. Based on Flory's theory for macromolecular solutions and gels, the swelling of such a grafted phase by a solvent is calculated. Results are applied to evaluate the partition coefficient of a solute between grafted molecules and a solvent. Variations of this coefficient with the molecular sizes of the solvent, solute, and grafts and with the interactions between these molecules are studied.

The behavior of a macromolecule in the vicinity of an interface is useful for understanding the adsorption of polymers[1-3] and for explaining the fractionation observed in gel permeation chromatography (GPC).[4-6]

In the particular case of a macromolecule attached by one of its ends to a surface, numerous applications are suggested: liquid–liquid chromatography, selective absorption of pollutants, compatibilization of prosthesis with blood, stabilization of polymer emulsions, supported catalysis, etc.

The thickness of the polymer layer adsorbed on a surface and its variation with molecular weight has been experimentally determined.[1,3] The segmental distribution of grafted macromolecules has been evaluated both theoretically and by simulation[7,12] but their thermodynamic characteristics have not been systematically studied. These characteristics should allow one to better understand the behavior of grafted materials. Hence, we investigated the problem and using Flory's theory on macromolecular solutions,[13,14] we calculated the swelling by a solvent of a macromolecular phase grafted on a plane and we deduced the partition coefficient of a solute between the two phases of such a system.[15]

Model

As depicted in Figure 1, we take as our model N_3 nonentangling polymer chains grafted onto an inert plane. That is, chains are independent and there is no adsorption effect on the wall.

According to the lattice liquid theory[13,14] solvent and polymer molecules are assumed to be constituted of segments of identical volume. Thus, each molecule of solvent is composed of r_1 segments and each molecule of polymer is composed of r_3 segments.

This rough model, representative of graft phases used in practice, requires the specification of only a few parameters and the resulting expressions can be easily applied to experimental data. For example, it elucidates the behavior of chemically bonded stationary phases which have gained increasing importance in liquid chromatography.

Free Energy of Mixtures

The free-energy change involved in the mixing of a solvent with the grafted phase is ΔF:

$$\Delta F = \Delta F_M + \Delta F_{EL} \tag{1a}$$

in which ΔF_M is the free energy of mixing

$$\Delta F_M = \Delta H_M - T\Delta S_M \tag{1b}$$

and ΔF_{EL} is the elastic free energy due to the molecular expansion of the grafted chains in the solvent.

1. Computing Entropy of ΔS_M Mix. Consider a solution consisting of N_1 molecules of solvent and N_3 molecules of polymer. The number of permissible patterns of the two kinds of molecules in such a system is Ω.

When the polymer molecules have one end attached to a surface, the pattern number becomes Ω'. Ω' is smaller than Ω:

$$\Omega' = \Omega PP' \tag{2}$$

P is the fraction of all the configurations that would still remain available if the position of one end of all the polymer molecules were fixed in the solution. P' is the fraction of these permissible configurations when all such fixed points are on a plane bounding the solution. The symbols Ω'_0, Ω_0, P_0, and P'_0 denote the corresponding quantities for pure compounds.

a. Calculating P. Using a lattice model, any solution of N_3 polymer molecules (r_3 segments) and N_1 solvent molecules (r_1 segments) comprises $N_1 + (r_3/r_1)N_3$ cells. We consider all the permissible configurations of this system. We can choose N_3 cells to be occupied by one polymer chain end. For each specific choice of N_3 cells, the number of permissible configurations is the same. Hence for a given choice of N_3 cells, the corresponding fraction of the total number of configurations is:

$$P = \frac{1}{C^{N_3}_{N_1+(r_3/r_1)N_3}} = \frac{N_3!\left[N_1 + N_3\left(\frac{r_3}{r_1} - 1\right)\right]}{\left[N_1 + N_3\frac{r_3}{r_1}\right]!} \tag{3}$$

For our purpose, a solution of N_3 one-end-bonded macromolecules and N_1 solvent molecules corresponds to a particular choice of N_3 cells. Thus P is derived from eq 3.

It follows that for pure compounds:

$$P_0 = \frac{N_3!\left[N_3\left(\frac{r_3}{r_1} - 1\right)\right]!}{(N_3[r_3/r_1])!} \tag{4}$$

b. Calculating P'. The fraction p'_x of all conformatins of a polymer chain (r_3 segments) that are still available when one end of the chain is fixed at a distance x of an impenetrable plane boundary has been evaluated by Casassa[16]

$$p'_x = \frac{2}{\pi^{1/2}}\int_0^{(x/2)(6/(r_3/r_1)b^2)^{1/2}} e^{-t^2}\,dt \tag{5}$$

in which b is the length of one of the r_3/r_1 units of the polymer chain.

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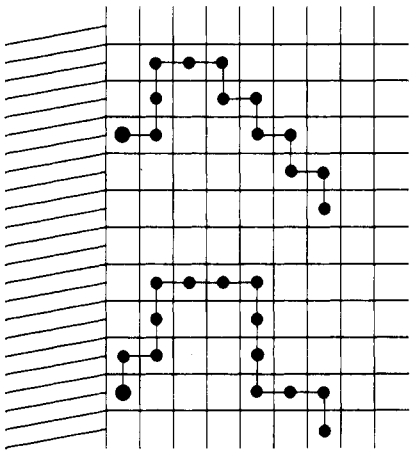

Figure 1. Depiction of grafted chains using a lattice model.

The flexible portion of a polymer chain terminally attached to a plane begins at a distance b from the plane. Thus we shall consider that in our case $x = b$, after which applying eq 5 gives $p'_{b,0}$, i.e.,

$$p'_{b,0} = \frac{2}{\pi^{1/2}}\int_0^{[(3/2)(r_1/r_3)]^{1/2}} e^{-t^2}\,dt = \mathrm{erf}\left(\frac{3}{2}\frac{r_1}{r_3}\right)^{1/2} \quad (6)$$

When the attached molecule is swollen by a solvent, its volume fraction is ϕ_3 and the average distance between two points of the chain is multiplied by $\phi_3^{-1/3}$. As the pinning distance is unmodified, Casassa's result leads to:

$$p'_{b,1} = \frac{2}{\pi^{1/2}}\int_0^{(b/2)[6/(r_3/r_1)b^2\phi_3^{-2/3}]^{1/2}} e^{-t^2}\,dt \quad (7)$$

$$p'_{b,1} = \frac{2}{\pi^{1/2}}\int_0^{[(3/2)(r_1/r_3)\phi_3^{2/3}]^{1/2}} e^{-t^2}\,dt = \mathrm{erf}\left(\frac{3}{2}\frac{r_1}{r_3}\phi_3^{2/3}\right)^{1/2}$$

Here, $p'_{b,0}$ and $p'_{b,1}$ refer to one molecule. When N_3 identical but non-entangling macromolecules are grafted, the total number of configurations is:

$$\Omega' = \Omega P(p'_{b,1})^{N_3} = \Omega PP'$$

c. Expression of the Entropy of Mixing ΔS_M. The expression of the entropy of mixing is:

$$\Delta S_M = K \ln \frac{\Omega'}{\Omega'_0} = K\left(\ln \frac{\Omega}{\Omega_0} + \ln \frac{P}{P_0} + N_3 \ln \frac{p'_{b,1}}{p'_{b,0}}\right) \quad (8)$$

According to Flory's lattice theory of polymer solutions,[13,14] the term $\ln (\Omega/\Omega_0)$ is expressed by $\ln (\Omega/\Omega_0) = -(N_1 \ln \phi_1 + N_3 \ln \phi_3)$. Substituting Stirling's approximations for the factorials appearing in the expressions for P and $p'_{b,1}$ leads after some simplification to:

$$\frac{\Delta S_M}{K} = -N_1 \ln \phi_1 + \left[N_3\left(\frac{r_3}{r_1} - 1\right) + N_1\right] \ln\left(1 - \frac{r_1}{r_3}\phi_3\right) - N_3\left(\frac{r_3}{r_1} - 1\right) \ln\left(1 - \frac{r_1}{r_3}\right) + N_3 \ln \frac{\mathrm{erf}\left(\frac{3}{2}\frac{r_1}{r_3}\phi_3^{2/3}\right)^{1/2}}{\mathrm{erf}\left(\frac{3}{2}\frac{r_1}{r_3}\right)^{1/2}} \quad (9)$$

2. Evaluating ΔS_{EL}. By analogy with Flory's theory on gels,[13,14] we must find the probability Ω_{EL} that the N_3 grafted chains will occur spontaneously in a specified conformation, following a deformation which is characterized by an expansion parameter α and is constrained in the following ways: the ends of $N_{3,i}$ chains are within a differential volume element $\Delta x\Delta y\Delta z$ located about point (xi,yi,zi); a chain end having components $(xi/\alpha,yi/\alpha,zi/\alpha)$ has components (xi,yi,zi) after deformation.

When the deformation process is swelling, $\alpha^3 = 1/\phi$ in which ϕ_3 is the volume fraction of the polymer in the swollen phase. The probability that any given grafted chain has components (zi,yi,zi) within the range $(\Delta x,\Delta y,\Delta z)$ is:

$$w_i = W(xi,yi,zi)\Delta x\Delta y\Delta z$$

in which

$$W(xi,yi,zi) = \frac{\beta^3}{\Pi^{3/2}} e^{-\beta^2(x!^2+y!^2+z!^2)} \quad (10)$$

and

$$\beta = (3/2)^{1/2}/\left(\frac{r_3}{r_1}\right)^{1/2} b$$

Flory's calculation for N_3 chains leads to:

$$\Omega_{EL} = N_3!\Pi_i \frac{w_i^{N_{3,i}}}{N_{3,i}!} \quad (11)$$

in which $N_{3,i}$ is given by

$$N_{3,i}(xi,yi,zi) = N_3 w\left(\frac{xi}{\alpha},\frac{yi}{\alpha},\frac{zi}{\alpha}\right)\frac{\Delta x\Delta y\Delta z}{\alpha^3} \quad (12)$$

Taking logarithms and introducing Stirling's approximation for the factorials:

$$\ln \Omega_{EL} = \sum_i N_{3,i} \ln \frac{w_i N_3}{N_{3,i}} \quad (13)$$

Substituting the summation by appropriate integrations we obtain

$$\ln \Omega_{EL} = N_3\alpha^3\frac{\beta^3}{\pi^{3/2}}\int_0^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \exp\left[-\frac{\beta^2}{\alpha^2}(x^2+y^2+z^2)\right] \times [\beta^2(1/\alpha^2 - 1)(x^2+y^2+z^2) + \ln \alpha^3]\,dx\,dy\,dz \quad (14)$$

i.e.,

$$\ln \Omega_{EL} = -\frac{N_3}{2}\left[\frac{3\alpha^2 - 3}{2} - \ln \alpha^3\right]$$

The entropy change involved in deformation is obtained by substracting from $k \ln \Omega_{EL}$ the value of S for $\alpha^3 = 1$:

$$\Delta S_{EL} = -\frac{kN_3}{2}\left[\frac{3\phi_3^{-2/3} - 3}{2} - \ln \phi_3^{-1}\right] \quad (15)$$

3. Computing Term ΔH_M. We can assume that the interaction energy between a polymer segment and a solvent molecule remains unchanged after grafting. Hence, ΔH_M is the classical enthalpy of mixing calculated by Flory:[13,14]

$$\Delta H_M = kT\chi_{13}N_1\phi_3 \quad (16)$$

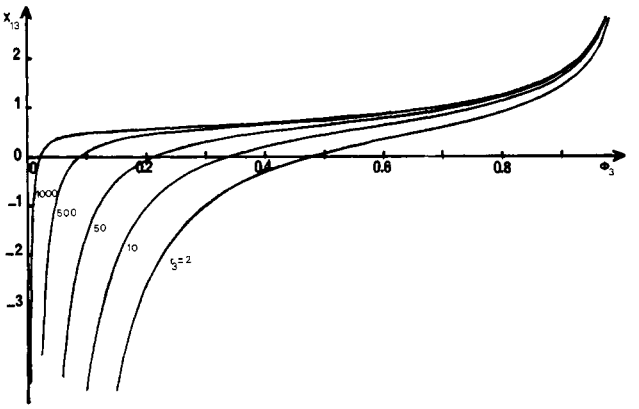

Figure 2. Swelling of grafted phase (ϕ_3) vs. χ_{13} for various values of r_3 and by taking $r_1 = 1$.

in which χ_{13} is Flory's interaction parameter.

4. Evaluating the Swelling. According to the previous equations the expression of ΔF_M is:

$$\Delta F_M = kT\left[N_1 \ln \phi_1 - \left[N_1 + N_3\left(\frac{r_3}{r_1} - 1\right)\right] \ln\left(1 - \frac{r_1}{r_3}\phi_3\right) + N_3\left(\frac{r_3}{r_1} - 1\right)\ln\left(1 - \frac{r_1}{r_3}\right) - N_3 \ln \frac{\operatorname{erf}\left(\frac{3}{2}\frac{r_1}{r_3}\phi_3^{2/3}\right)^{1/2}}{\operatorname{erf}\left(\frac{3}{2}\frac{r_1}{r_3}\right)^{1/2}} + \frac{N_3}{2}\left[\frac{3\phi_3^{-2/3} - 3}{2} - \ln \phi_3^{-1}\right] + \chi_{13}N_1\phi_3\right] \quad (17)$$

Hence solvent activity in the swollen phase is:

$$\ln a_1 = \frac{\mu_1 - \mu_1^0}{kT} = \frac{1}{kT}\left(\frac{\partial \Delta G_M}{\partial N_1}\right)$$

It follows that:

$$\ln a_1 = \ln(1 - \phi_3) + \phi_3\left(1 - \frac{r_1}{r_3}\right) - \ln\left(1 - \phi_3\frac{r_1}{r_3}\right) + \frac{r_1}{2r_3}(\phi_3^{1/3} - \phi_3) + \frac{1}{\operatorname{erf}\left(\frac{3}{2}\frac{r_1}{r_3}\phi_3^{2/3}\right)^{1/2}} \times \phi_3^{4/3}\left(\frac{2}{3\pi}\left(\frac{r_1}{r_3}\right)^3\right)^{1/2} e^{-(3/2)(r_1/r_3)\phi_3^{2/3}} + \chi_{13}\phi_3^2 \quad (18)$$

At the swelling equilibrium, $\ln a_1 = 0$. In Figure 2, χ_{13} is plotted against ϕ_3 for each value of r_3 ($r_1 = 1$). We mention that the swelling of the grafted phase increases with r_3 and decreases with χ_{13}.

Calculation of the Partition Coefficient K_D of a Macromolecular Solute between a Grafted Polymer and a Solvent

1. Free-Energy Formula. Extension of the previous equations to a system of three components, using r_2, for example, to characterize the solute, leads to the free-energy change ΔF involved in the mixing of a solute with the swollen grafted phase:

$$\Delta F_M = \Delta H_M - T(\Delta S_M + \Delta S_{EL})$$

in which

$$\Delta H_M = \chi_{13}N_1\phi_3 + \chi_{12}N_1\phi_2 + \chi_{23}r_3N_3\phi_2 \quad (19)$$

and

$$\Delta S_{EL} = -\frac{kN_3}{2}\left(\frac{3\alpha^2 - 3}{2} - \ln \alpha^3\right) \quad (20)$$

χ_{12} is Flory's solvent/solute interaction parameter and χ_{23} represents the interaction intensity between a segment of the grafted chains and a segment of the solute.

2. Computing ΔS_M. According to Flory's theory,[13,14] if the ternary system were composed of N_1 solvent molecules, N_2 solute molecules, and N_3 chains in solution, the total number of configurations of this system would be

$$\ln(\Omega/\Omega_0) = -[N_1 \ln \phi_1 + N_2 \ln \phi_2 + N_3 \ln \phi_3] \quad (21)$$

It has been shown above that Ω becomes Ω' when the N_3 polymer molecules are actually grafted on a plane:

$$\Omega' = \Omega PP'$$

Disregarding the steric constraint of the wall, the distribution of the solute in the grafted phase would be homogeneous.

Assuming the grafted phase to be a layer of a swollen polymer of thickness e, the probability of finding one end of a solute molecule between distances x and $x + dx$ from the wall is $d\Omega' = \Omega\, dx/e$.

In fact the vicinity of the wall decreases this number of permissible configurations by the factor p'_x. According to Casassa's calculation:

$$p'_x\, d\Omega' = \frac{2}{\pi^{1/2}}\left[\int_0^{(x/2b)(6r_1/r_2)^{1/2}} e^{-t^2}\, dt\right]\frac{\Omega}{e}\, dx \quad (22)$$

Assuming thickness e of the grafted phase to be the diameter of the equivalent sphere of a dissolved macromolecule having the same swelling as the grafted macromolecule, then

$$e = \alpha\left(\frac{r_3}{r_1}\right)^{1/2} b$$

Extenting the steric effect of the wall to all the grafted molecules, the total number of permissible arrangements Ω'' of the solute becomes

$$\Omega'' = \left[\int_0^{\alpha(r_3/r_1)^{1/2}b} \frac{2}{\pi^{1/2}}\int_0^{(x/2b)(6r_1/r_2)^{1/2}} e^{-t^2}\, dt\, dx\right] \times \frac{\Omega'}{\alpha(r_3/r_1)^{1/2}b} = p''_1\Omega' \quad (23)$$

After integration one finds

$$p''_1 = \operatorname{erf}\left[\phi_3^{-1/3}\left(\frac{3}{2}\frac{r_3}{r_2}\right)^{1/2}\right] + \phi_3^{1/3}\left(\frac{2}{3\pi}\frac{r_2}{r_3}\right)^{1/2}\left[e^{-[(3/2)(r_3/r_2)\phi_3^{-2/3}]} - 1\right] \quad (24)$$

It follows that

$$\Delta S_M = k\left[\ln\frac{\Omega}{\Omega_0} + \ln\frac{P}{P_0} + N_3 \ln\frac{p'_{b,1}}{p'_{b,0}} + N_2 \ln p''_1\right] \quad (25)$$

Lastly,

$$\frac{\Delta S_M}{k} = -N_1 \ln\phi_1 - N_2 \ln\phi_2 + \left[N_3\left(\frac{r_3}{r_1} - 1\right) + N_1\right]\ln\left(1 - \frac{r_1}{r_3}\phi_3\right) - N_3\left(\frac{r_3}{r_1} - 1\right)\ln\left(1 - \frac{r_1}{r_3}\right) + N_3 \ln\left[\frac{\operatorname{erf}\left(\frac{3}{2}\frac{r_1}{r_3}\phi_3^{2/3}\right)^{1/2}}{\operatorname{erf}\left(\frac{3}{2}\frac{r_1}{r_3}\right)^{1/2}}\right] + N_2 \ln\left\{\operatorname{erf}\left(\phi_3^{-1/3}\left(\frac{3}{2}\frac{r_3}{r_2}\right)^{1/2}\right) + \phi_3^{1/3}\left(\frac{2}{3\pi}\frac{r_2}{r_3}\right)^{1/2}[e^{-(3/2)(r_3/r_2)\phi_3^{-2/3}} - 1]\right\} \quad (26)$$

3. Computing the Partition Coefficient K_D. From the previous equations one finds the activity of the solute in the grafted phase and in the solvent. The following substitutions can be made assuming the solute is considered as very dilute:

$$\phi_2 \simeq \phi'_2 \simeq 0$$

$$\phi'_1 \simeq 1$$

Hence,

$$\ln a_2 = \frac{\mu_2 - \mu_2^0}{kT} \simeq \frac{1}{kT}\frac{\partial \Delta G_M}{\partial N_2} = \ln\phi_2 + 1 - \frac{r_2}{r_1}\phi_1 - \frac{r_2}{r_3}\phi_3 - \left[\ln\left(1 - \frac{r_1}{r_3}\phi_3\right)\right]r_2 + \frac{r_2}{2r_3}[\phi_3^{1/3} - \phi_3] - \ln\left[\operatorname{erf}\left(\phi_3^{-2/3}\frac{3}{2}\frac{r_3}{r_2}\right)^{1/2} + \left(\frac{2}{3\pi}\frac{r_2}{r_3}\right)^{1/2}\phi_3^{1/3}[e^{-[(3/2)(r_3/r_2)\phi_3^{-2/3}]} - 1]\right] + \frac{1}{\operatorname{erf}\left(\frac{3}{2}\frac{r_1}{r_3}\phi_3^{2/3}\right)^{1/2}}e^{-[(3/2)(r_1/r_3)(1/\phi_3^{-2/3})]}\phi_3^{4/3}\left(\frac{2}{3\pi}\frac{r_1r_2^2}{r_3^3}\right)^{1/2} + \chi_{12}\frac{r_2}{r_1}\phi_1 + \chi_{23}r_2\phi_3 - \chi_{13}\frac{r_2}{r_1}\phi_1\phi_3 \quad (27)$$

and

$$\ln a'_2 = \frac{\mu'_2 - \mu'^0_2}{kT} = \ln\phi'_2 + 1 - \frac{r_2}{r_1} + \chi_{12}\frac{r_2}{r_1} \quad (28)$$

The condition $a_2 = a'_2$ must be satisfied to arrive at equilibrium of the solute between the two phases. This equality gives the expression for the ratio $\ln K_D \simeq \phi_2/\phi'_2$:

$$\ln K_D \simeq -r_2\left(\frac{1}{r_1} - \frac{1}{r_3}\right)\phi_3 - \frac{(\phi_3^{1/3} - \phi_3)}{2}\frac{r_2}{r_3} + \ln\left(1 - \frac{r_1}{r_3}\phi_3\right)r_2 + \chi_{12}\frac{r_2}{r_1}\phi_3 + \chi_{13}\frac{r_2}{r_1}\phi_1\phi_3 - \chi_{23}r_2\phi_3 - \frac{\left(\frac{2}{3\pi}\frac{r_1r_2^2}{r_3^3}\right)^{1/2}\phi_3^{4/3}}{\operatorname{erf}\left(\frac{3}{2}\frac{r_1}{r_3}\right)^{1/2}\phi_3^{1/3}}e^{-[(3/2)(r_1/r_3)\phi_3^{2/3}]} + \ln\left[\operatorname{erf}\left(\phi_3^{-1/3}\left(\frac{r_3}{r_2}\frac{3}{2}\right)^{1/2}\right) + \left(\frac{2}{3\pi}\frac{r_2}{r_3}\right)^{1/2}\phi_3^{1/3}(e^{-[(3/2)(r_3/r_2)\phi_3^{-2/3}]} - 1)\right] \quad (29)$$

Discussion

Partition coefficient K_D is a function of the size of the three different kinds of molecules. It largely depends on the relative magnitude of the interaction terms χ_{ij}. If there is no enthalpic effect ($\chi_{ij} = 0$), K_D varies from 0 to 1 as the molecular weight of the solute decreases from ∞ to 0. Figure 3, in which the logarithm of the molecular weight of the solute (M_2 taken as 100 r_2) is plotted versus K_D, illustrates this prediction. The curves are similar to the calibration curves of gel permeation chromatography.[24] The solubility of high molecular weight solutes increases with the molecular weight of the grafted chains.

The role of the solvent depends not only on the size of its molecules but mainly on its interactions with the solute and the gel (χ_{12} and χ_{13}). When we consider a series of solvents all of which swell the grafted molecules identically (i.e., the grafted molecules/solvent interactions are constant) but which have various affinities for the solute, the solubility of the solute into the grafted phase can be appreciably altered as shown on Figure 4. In this figure, curves for the logarithm of the molecular weight ($M_2 = 100r_2$) as a function of K_D are plotted for the values $\chi_{13} = \chi_{23} = 0$, $\chi_{12} = 0$ (or 0.5), $r_3 = 10$, and $r_3 = 500$.

On the other hand, as the affinity of the solute toward the grafted phase increases (i.e., for decreasing values of χ_{23}), the curves $\log M_2 = f(K_D)$ become warped and particularly when the solute/grafted chain interactions are very strong K_D becomes greater than 1. Figure 5 shows the change for $\chi_{13} = 0.5$, $\chi_{12} = 0$, and $r_3 = 10$.

Validity of the Proposed Model

Our calculations are based on the lattice theory of polymer solutions developed by Flory[13,14] and by Huggins.[17] The theory assumes that the interactions between the various species do not permit the formation of complexes which cannot easily be dissociated by thermal agitation at the experimental temperature (hypothesis of "regular" systems). It is also assumed that χ_{13} values are independent of ϕ_3, which is not always valid.[18]

Several assumptions on the nature of the grafted phase have been made. The number of configurations has been calculated assuming $r_3/r_1 >> 1$. The Surface bonded to the grafted chains is equated with an inert plane, i.e., it does not constrain segments of the grafted molecules to lie along it preferentially. As a general rule, we assume that no adsorption occurs at the various interfaces of the system. In practice the validity of this assumption depends largely on the nature of grafts, surface, and solvent.[1,3] For polystyrene deposit on silica, it has been shown experimentally that even in a Θ solvent, the greater part of the

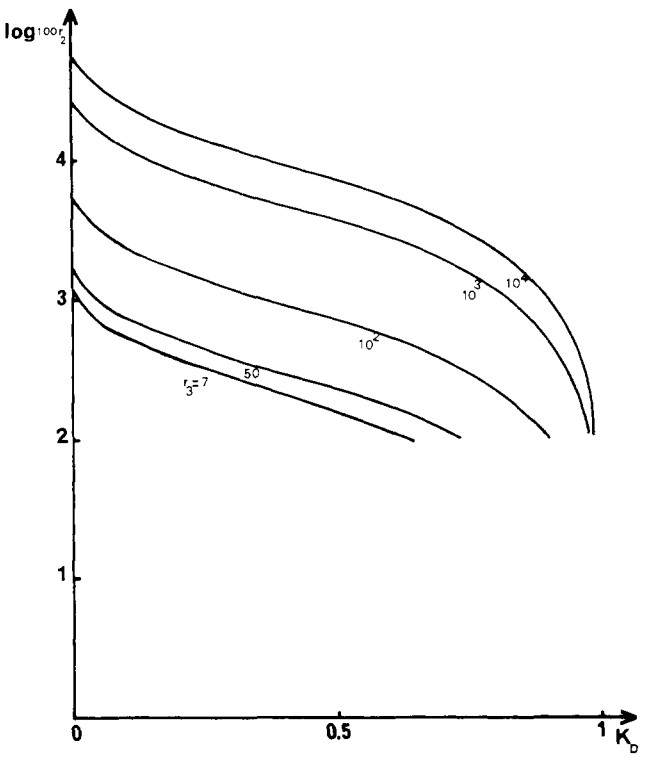

Figure 3. log M_2 (M_2 taken as $100r_2$) vs. K_D (partition coefficient) for various values of r_3. Curves plotted with $r_1 = 1$ and $\chi_{12} = \chi_{13} = \chi_{23} = 0$.

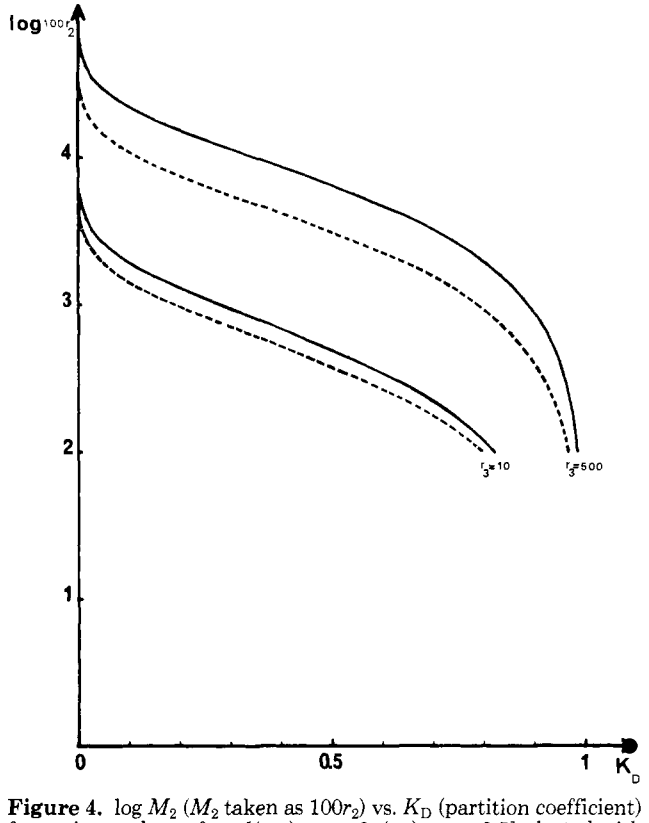

Figure 4. log M_2 (M_2 taken as $100r_2$) vs. K_D (partition coefficient) for various values of χ_{12} [(---) $\chi_{12} = 0$, (—) $\chi_{12} = 0.5$] plotted with $r_3 = 10$ or 500 and $\chi_{13} = \chi_{23} = 0$.

segments of the adsorbed polymer molecules are far from the adsorbing surface and the thickness of the adsorbed layer varies like the radius of gyration of a macromolecule in solution.[19-21]

The grafting of a macromolecular chain increases its extension perpendicular to the plane. The opposite effect

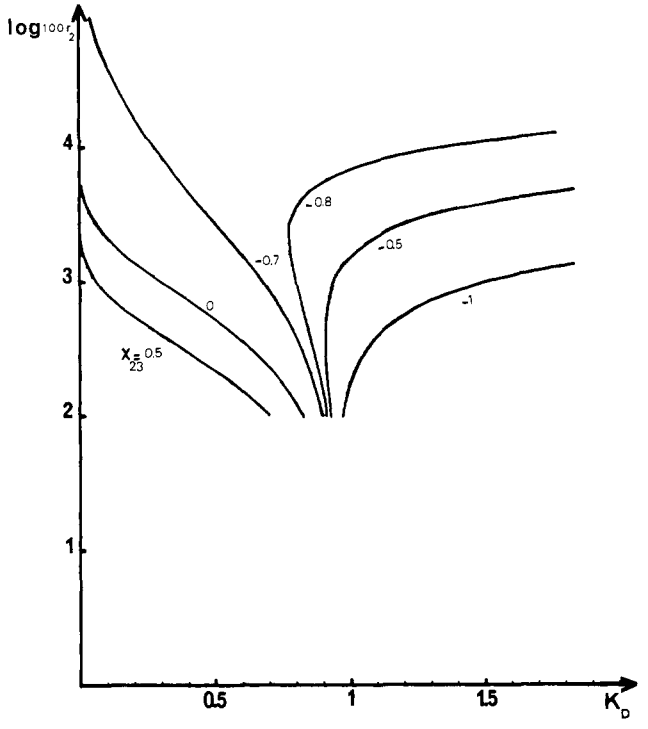

Figure 5. log M_2 (M_2 taken as $100r_2$) vs. K_D (partition coefficient) for various values of χ_{23}. Curves plotted with $r_3 = 10$ and $\chi_{12} = \chi_{13} = 0$.

is observed when adsorption of the macromolecule occurs on the surface. Smitham and Napper[19] found that the thickness of the attached layer corresponds to 2–2.5 times the unperturbed end-to-end distance of a polymer chain (i.e., $2b(r_3/r_1)^{1/2}$. Experimental results of Dorokowski and Lambourne[22] lead to a thickness for the attached layer varying from $0.43b(r_3/r_1)^{1/2}$ to $2.7b(r_3/r_1)^{1/2}$. For our calculation we chose $\alpha\ b(r_3/r_1)^{1/2}$.

The distribution of polymer segments into the grafted phase is assumed to be homogeneous. A factor expressing the correction for inhomogeneity of the solution can be introduced, but mathematical expressions would be considerably more complicated.[7,23]

The expressions proposed for the swelling and for the partition coefficient K_D obtained for the grafted phases should be compared with those which were calculated for gels.[24] Substituting the length between two cross-linkages of the gel for the length of the grafted molecules, the behavior of grafted materials and of gels appears to be similar. Hence, as for gels, our results should allow one to better understand the separation mechanisms on grafted phases involved in liquid–liquid chromatography. Such experimental studies have been performed in our laboratory.[15,25,26]

References and Notes

(1) F. R. Eirich, *J. Colloid Interface Sci.*, **58**, 432 (1977).
(2) Yu S. Lipatov and L. M. Sergeeva, "Adsorption of Polymers", Wiley, New York, 1974.
(3) P. G. De Gennes, *J. Phys.*, **37**, 144, 5 (1976).
(4) E. F. Casassa, *J. Phys. Chem.*, **75**, 3929 (1971).
(5) F. Verhoff and N. Sylvester, *J. Macromol. Sci. Chem.*, **4**, 979 (1970).
(6) C. Guttmann and E. Dimarzio, *Macromolecules*, **3**, 681 (1970).
(7) T. A. Weber and E. Helfand, *Macromolecules*, **9**, 311 (1976).
(8) D. J. Meier, *J. Phys. Chem.*, **71**, 1861 (1967).
(9) F. Hesselink, *J. Phys. Chem.*, **73**, 3488 (1969).
(10) M. Lax, *Macromolecules*, **7**, 660 (1974).
(11) E. J. Clayfield and E. C. Lumb, *J. Colloid Interface Sci.*, **20**, 285 (1966).
(12) T. Tanaka, *Macromolecules*, **10**, 51 (1977).
(13) P. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

(14) P. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953.
(15) J. Lecourtier, Thèse de Doctorat d'Etat, Universite P. et M. Curie, Paris, Dec. 19, 1977.
(16) E. F. Casassa, *Sep. Sci.*, **6** (2), 305 (1971).
(17) M. Huggins, *Ann. N.Y. Acad. Sci.*, **43**, 1 (1942).
(18) P. Rempp in "Reactions on Polymers", J. A. Moore, Ed., Dordrecht, Boston, 1973, p 265.
(19) J. B. Smitham and D. H. Napper, *J. Polym. Sci., Polym. Symp.*, **55**, 51 (1976).
(20) R. Stromber, E. Passaglia, and D. J. Tutas, *J. Res. Natl. Bur. Stand., Sect. A*, **67**, 431 (1963).
(21) G. Gebhard and E. Killmann, *Angew. Makromol. Chem.*, **53**, 71 (1976).
(22) A. Doroszkowski and R. Lambourne, *J. Colloid Interface Sci.*, **43**, 97 (1973).
(23) E. Helfand, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **15**, 216 (1975).
(24) J. Lecourtier, R. Audebert, and C. Quivoron, *J. Chromatogr.*, **121**, 173 (1976).
(25) J. Lecourtier, R. Audebert, and C. Quivoron, *J. Liq. Chromatogr.*, **1**, 367 (1978).
(26) J. Lecourtier, R. Audebert, and C. Quivoron, *J. Liq. Chromatogr.*, **1**, 479 (1978).

Conformation of Block Copolymers in Dilute Solution. 3. Determination of the Center-to-Center Distance between the Two Blocks by Light Scattering[1]

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ABSTRACT: The conformation of an AB diblock copolymer in dilute solution may be characterized by the mean-square radii $\langle S^2\rangle_A$ and $\langle S^2\rangle_B$ of the two blocks and the mean-square distance $\langle G^2\rangle$ between the centers of mass of them. It was previously established that $\langle S^2\rangle_K$ (K = A or B) is almost identical with the radius $\langle S^2\rangle_{H\text{-}K}$ of the equivalent K homopolymer, unless the A–B interactions are attractive. In such a situation, it is possible to determine $\langle G^2\rangle$ by light scattering with a solvent having large refractive index increments for the two homopolymers. Experiments were conducted on polystyrene–poly(methyl methacrylate) diblock copolymers in 2-butanone. The parameter σ representing the extent of "segregation" of the two blocks, $\sigma = \langle G^2\rangle/(2\langle S^2\rangle_A + 2\langle S^2\rangle_B)$, was evaluated with due regard to the sample heterogeneity. The influence of heterogeneity was found to be unexpectedly large even for a fairly homogeneous sample, say $M_w/M_n < 1.1$, and without adequate correction to this effect, the conclusion drawn from such an analysis could be misleading. It was found that σ lies very close to 1.2. This shows that the conformation of the block copolymer is almost the same as that of the homopolymers. Models like "segregated" and "core-in-shell" conformations are utterly at variance with reality.

Despite the enormous effort so far made to understand the chain conformation of block copolymers in dilute solution, the progress until recently has been highly unsatisfactory.[2a] This is due, on the one hand, to crucial difficulties of dealing with the problem theoretically[2b] and, on the other hand, to lack of effective experimental techniques which provide unequivocal information. This situation has given rise to considerable confusion regarding the simplest picture of block copolymer conformation, and thus various models, typified by the "quasi-random coil", "segregated", and "core-in-shell" conformations, have been proposed, without clear definitions for them.[1]

Very recently, considerable success has been gained by computer "experiments".[3-6] One of the important conclusions drawn thereby[3] was that the mean-square radius $\langle S^2\rangle_K$ (K = A or B) of the individual block in an AB diblock copolymer is almost the same as the radius $\langle S^2\rangle_{H\text{-}K}$ of the equivalent K homopolymer, insofar as the A–B interactions are assumed to be nonattractive. More precisely, it was shown that the ratio γ_K given by

$$\gamma_K = \langle S^2\rangle_K/\langle S^2\rangle_{H\text{-}K} \qquad (K = A \text{ or } B) \qquad (1)$$

ranges from 1.00 to 1.02 in a common good or Θ solvent for the two homopolymers.[7] Existing Monte-Carlo data on homopolymers[3] and those on block copolymers recently reported by Bendler et al.[5] are quite consistent with this conclusion.

Interestingly, an artificial "segregated" chain which was simulated by a random walk biased by the presence of an impermeable, noninteracting plane passing through the A–B junction was found to give a value of $\gamma_K = 1.03$.[8]

The parameter γ_K can be unambigously determined by light-scattering experiments: For a *homogeneous* diblock copolymer, the light-scattering apparent radius $\langle S^2\rangle_{app}$ is given by

$$\langle S^2\rangle_{app} = \mu_A\langle S^2\rangle_A + \mu_B\langle S^2\rangle_B + \mu_A\mu_B\langle G^2\rangle$$
$$\mu_A = 1 - \mu_B = x_A\nu_A/(x_A\nu_A + x_B\nu_B) \qquad (2)$$

where $\langle G^2\rangle$ is the mean-square distance between the centers of mass of the two blocks, and x_K and ν_K are the weight fraction and the refractive index increment of the K block, respectively. With a solvent in which $\nu_B = 0$, for example, we have $\langle S^2\rangle_A$ ($=\langle S^2\rangle_{app}$). Obviously, this method is applicable also to a heterogeneous block copolymer, for which the z-average radius of the A block is obtained. An analysis of existing light-scattering data of this kind led to the conclusion that γ_K is unity within an experimental uncertainty of, say, ±10%.[3] More recent neutron-scattering data of Benoit et al.[9,10] appear to be consistent with this conclusion. As far as we are aware, the only counterevidence for this is found in the paper of Han and Mozer.[11a] However, these experiments seem to leave room for criticism.[11b]

For all these reasons, it is firmly believed that γ_K is, in a practical sense, equal to unity for a block copolymer showing repulsive interactions between the two blocks. Under such a situation, eq 2 may be well approximated by

$$\langle S^2\rangle_{app} = \mu_A\langle S^2\rangle_{H\text{-}A} + \mu_B\langle S^2\rangle_{H\text{-}B} + \mu_A\mu_B\langle G^2\rangle \qquad (3)$$

With independently determined values of $\langle S^2\rangle_{H\text{-}K}$, we can

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