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Polymer Adsorption at the Oil-Water Interface

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A general theory of polymer adsorption at a semi-permeable oil-water interface of the biphasic solution is presented. The configurational factor of the solution in the presence of the semi-open boundary at the interface is evaluated by the quasi-crystalline lattice model. The present theory gives the feature of the bulk concentration equilibria between oil-water subsystems and the surface excesses of Γ^α and Γ^β of the polymer segments as a function of the degree of polymerization r, the Flory-Huggins parameter in β-phase x_p^β, the differential adsorption energy parameter in β-phase x_σ^β, the differential interaction energy parameter Δx_p and the bulk concentration of the polymer in β-phase $\varphi_2^{\beta(*)}$. From our numerical results, the characteristics of Γ^α are shown to be significantly different from those of Γ^β in the case of high polymers, and this would be the most apparent feature of the adsorption behavior of the polymer at a semi-permeable oil-water interface, which is sensitively dependent on Δx_p and r.

Introduction

The adsorption behavior of the polymer at an interface from its solution is of great importance in theoretical and practical aspects, and it plays an essential role in colloid science, such as adhesion, flocculation, stablization and destabilization of colloid particles by polymeric additives. But, there have been comparatively little researches concerned with the adsorption of polymer molecules at a "*semi-permeable*" liquid-liquid interface which only the solute molecules can penetrate. Most of researches[1-7] in adsorption phenomena of the polymer have been confined to the adsorption behavior at the impermeable interface from binary polymer solution. Recently, Halperin and Pincus[8] have developed a theory of adsorption behavior at a liquid-liquid interface based on the van der Waals-Cahn-de Gennes theory.[9-12] This theory, though presenting the semi-quantitative descriptions of the adsorption behavior, comprehensively made the theoretical demonstration of the polymer adsorption behavior at a liquid-liquid interface.

In the case of a ternary mixture consisting of the polymer and the biphasic solvents, the adsorption behavior of the polymer at a semi-permeable liquid-liquid interface may be quite different from the corresponding case of impermeable interface and significantly pertaining to wetting behavior, stabilization of emulsion and colloidal dispersion by polymeric additives, etc. Each walk of a polymer chain near or at the interface is considerably influenced by its solubility factors determined by the biphasic solvents. Therefore, unlike the feature of an impermeable interface, at only one side of which the polymer adsorption takes place, the possible segmental walk of a polymer chain at the semi-permeable liquid-liquid interface under consideration may be allowed for passing through the interface from one phase into another. From the results of our numerical calculation, the adsorption amount of the polymer in poor phase is considerably recognizable even when its solubility in poor solvent is extremely small, and its adsorption behavior in poor phase is significantly different from that in good phase.

In this paper, we present a general theory of polymer adsorption from its biphasic solutions at a semi-permeable liquid-liquid interface. Our theory is based on a quasi-crystalline lattice model consisting of lattice layers parallel to the interface. The expression for the configurational term of present system is derived by a lattice statistics closely similar to the one used by Flory[13,14] in his works of Flory-Huggins lattice model of ideal polymer solution. The lattice model in our theory has a semi-open boundary at the interface. Therefore, at first we derive a general expression for the configurational term of the arbitrary lattice and apply this general expression to the present system. This procedure is closely similar to the one used in comprehensive lattice model of the polymer adsorption at an impermeable interface by Roe,[4] but the reference state of each phase in our system corresponds to its bulk polymer solution instead of the amorphous polymer state as assumed in ealier lattice theories.[4,6]

Theory

Model and Approximations. At first we consider a ternary mixture system consisting of a monodisperse polymer and two immiscible solvents. Then, there is a semi-permeable liquid-liquid interface formed by the biphasic solvents, through which the penetration of the solute molecules is exclusively allowed. In order to simplify the theoretical approach of our work, the present system is assumed to be confined to the normal liquid solution type. Therefore, we adapt the usual quasi-crystalline lattice model and the Bragg-Williams approximation of random mixing. Thus (i) the lattice type is completely conserved through the entire system. (ii) The size effects of the dissimilar solvents are assumed to be of no significance, and the size of a solvent molecule in one phase and that of a polymer segment are assumed to be equal to that of a solvent molecule in another phase. (iii) The flexibility of a polymer chain is conserved not only in each bulk phase of the system but also near the interface.

The system under consideration consists of a ternary mixture of N_1^α of α-solvent molecules, N_1^β of β-solvent molecules and N_2 polymer molecules of *r*mer in the presence of a planar liquid-liquid interface of area A. β-phase is currently defined as the good solvent-based phase (oil), and α-phase comparatively as the poor solvent-based one (water). The lattice is divided into layers of lattice sites parallel to the interface, labeled by the numerical order from the interface to each phase, so that

$$\alpha\,(i) = \alpha(1),\quad \alpha\,(2),\quad \cdots,\quad \alpha\,(M)\quad (\alpha\text{-phase}) \tag{1}$$

$$\beta\,(i) = \beta(1),\quad \beta(2),\quad \cdots,\quad \beta\,(M')\quad (\beta\text{-phase}) \tag{2}$$

where, for example, $\alpha(i)$ simply designates *i*th layer labeled from the interface in α-phase. Each layer consists of L lattice sites, so that

$$A = aL \tag{3}$$

where a is the contact area per monomer molecule, and

$$(M+M')\cdot L = N_1^\alpha + N_1^\beta + rN_2. \tag{4}$$

If *z* is the coordination number of the lattice, a lattice site in each layer has *z* nearest neighbors, of which *lz* are in the same layer and *mz* are in each of the adjacent layers, that is, $l+2m=1$.

The volume fractions of three components in layer $\alpha(i)$ or β-(i) are accordingly written as

$$\varphi_1^{\pi(i)} = \frac{n_1^{\pi(i)}}{L},\quad \varphi_2^{\pi(i)} = \frac{n_2^{\pi(i)}}{L},\quad \text{for}\quad \pi=\alpha,\ \beta, \tag{5}$$

where $n_1^{\pi(i)}$ and $n_2^{\pi(i)}$ are the numbers of the solvent molecules and the polymer segments in layer $\pi(i)$. Far from the interface, these volume fractions approach the equilibrium bulk volume fractions $\varphi_1^{\pi(*)}$ and $\varphi_2^{\pi(*)}$ for $\pi=\alpha$, β, respectively.

Partition Function. The formulation of the partition function corresponding to the whole ternary mixture system is somewhat complicated because there is a planar boundary dividing the biphasic subsystems. Therefore, instead, we define the equilibrium canonical partition functions corresponding to each of two subsystems divided by the interface, respectively. The equilibrium canonical partition function $Q^\pi(T, V, A, \varphi_1^{\pi(*)}, \varphi_2^{\pi(*)}, \{\varphi_1^{\pi(i)}; \varphi_2^{\pi(i)}\})$ corresponding to π-subsystem can be written as

$$Q^\pi = Q_1^\pi \cdot Q_2^\pi \cdot \Omega^\pi \cdot \exp(-U^\pi/KT),\qquad \text{for}\quad \pi=\alpha,\ \beta. \tag{6}$$

Here Q_1^π corresponds to the partition function of pure monomer liquid consisting of N_1^π molecules and Q_2^π the same for pure polymer liquid. Ω^π is the configurational factor which gives the expectation number or π-subsystem and will be derived in details in the next section. The energy term U^π of π-subsystem in *eqn* 6 gives the expression of the interaction of solvent-polymer segement pairs both in bulk phase and at the interface, including the repulsion factor between dissimilar α-β solvent pairs at the interface. Thus, U^α in α-phase can be written as

$$U^\alpha = L\cdot\{u_{\sigma o}^{\alpha\beta}\cdot\varphi_1^{\alpha(1)} + u_{\sigma p}^{\beta}\cdot\varphi_2^{\alpha(1)}\}\cdot\varphi_1^{\beta(1)} + LkT\cdot\chi_p^\alpha \sum_{i=1}^{M}\varphi_1^{\alpha(i)}\sum_{\nu=-1}^{1}\lambda_\nu\,\varphi_2^{\alpha(i+\nu)} \tag{7}$$

where $u_{\sigma o}^{\alpha\beta}$ corresponds to the repulsion energy between dissimilar solvents (α-solvent and β-solvent) at the interface, $u_{\sigma p}^{\beta}$ the interaction energy between a polymer segment and a β-solvent molecule at the interface, χ_p^α the Flory-Huggins interaction energy parameter in α-phase, $\lambda_{\pm1}=m$, and $\lambda_0=l$, respectively. Similarly, in β-phase, we have

$$U^\beta = L\cdot\{u_{\sigma o}^{\beta\alpha}\cdot\varphi_1^{\beta(1)} + u_{\sigma p}^{\alpha}\cdot\varphi_2^{\beta(1)}\}\cdot\varphi_1^{\alpha(1)} + LkT\cdot\chi_p^\beta \sum_{i=1}^{M'}\varphi_1^{\beta(i)}\sum_{\nu=-1}^{1}\lambda_\nu\,\varphi_2^{\beta(i+\nu)}, \tag{8}$$

where the parameters in *eqn* 8 can be defined by the same manner in *eqn* 7. From the approximation that the lattice type is conserved through the whole system as mentioned previously, namely, $\lambda_\nu^\alpha = \lambda_\nu^\beta$ for the same value of ν, we assume that the interaction type is conserved even at the interface as well as in each of the bulk phases.
Therefore, we have

$$u_{\sigma o}^{\alpha\beta}/kT = u_{\sigma o}^{\beta\alpha}/kT \cong \chi_o, \tag{9}$$

$$u_{\sigma p}^{\alpha}/kT = m\chi_p^\alpha,\qquad u_{\sigma p}^{\beta}/kT = m\chi_p^\beta. \tag{10}$$

Derivation of Ω^π. Each possible walk of a polymer chain for consecutive placements on the lattice sites in each of the adsorption layers is determined by the concentrations of the polymer segments not only in the same layer but also in the adjacent layers. Furthermore, the walk of a polymer chain at the interface under consideration is allowed for passing through the interface from one phase to another, according to not only its solubility factor determined by the difference of interaction energy between two phases but also the concentrations of the polymer segments in the first layers of two biphasic subsystems. Since the feature of each subsystem in this ternary system is closely similar to that of the adsorption behavior at an impermeable interface from the simple binary liquid mixtures only except the semi-open planar boundary of the interface in this system, we derive a general expression for Ω^π of binary polymer solution consisting of the concentration distribution of the adsorption layers with an arbitrary planar semi-open boundary at the interface. For practical conveniences, we adapt the Roe's procedure[4] because of its comprehensibility.

We write

$$\Omega = \frac{1}{N_2!}\cdot\prod_{K=1}^{N_2}\omega_k \tag{11}$$

where w_k is the expecting number of ways of placing a *r*mer molecule after $(k-1)$ *r*mer molecules have already been occupied on the lattice. We consider *i*th adsorption layer, on which $\varepsilon_{i,k-1}$ segments have been previously occupied. The number of ways for arranging *k*th polymer molecule, then, can be written as

$$\omega_k = [\prod_{i=1}^{M} \prod_{\varepsilon_i=0}^{\varepsilon_{i,k-1}} \omega_k^i] \cdot \prod_{j=2}^{r} \omega_{k,j} \tag{12}$$

where w_k^i is the number of ways for arranging $\varepsilon_{i,k-1}$ segments randomly on ith adsorption layer and $w_{k,j}$ is the number of ways for possible walks according to the concentration distribution of the polymer segments in the adsorption layers.

The number of possible placements of the first segment of kth polymer molecule on ith adsorption layer is simply obtained as

$$\omega_{k,1}^i = (L - \varepsilon_{i,k-1}) \tag{13}$$

where $\varepsilon_{i,k-1}$ is the number of polymer segments which have already been placed after (k-1)th polymer molecules occupied the adsorption layers. If we define $i(k,j)$ by the layer number on which the jth segment of the kth polymer molecule is placed, then the number of possible sites available to arrangement by the second segment is obtained as

$$\begin{aligned}\omega_{k,2} &= (mf_{i(k,1)-1} + lf_{i(k,1)} + mf_{i(k,1)+1}) \cdot z \\ &= z \cdot \sum_{\nu=-1}^{1} \lambda_\nu f_{i(k,1)+\nu}\end{aligned} \tag{14}$$

Similarly, for the number of possible placements of the jth segment for $j \geq 3$, we obtain

$$w_{k,j} = z' \sum_{\nu=-1}^{1} \lambda_\nu f_{i(k,j)+\nu}, \tag{15}$$

where $f_{i(k,j)}$ is defined as the expectancy that a site on the $i(k,j)$th layer, adjacent to the jth segment, is vacant, and $z' \equiv z$-1 for the ideal flexible polymer chain as proposed by Flory.[13,14] Thus, w_k is obtained as

$$\omega_k \cong [\prod_{i=1}^{M} (L - \varepsilon_{i,k-1})] \cdot \prod_{j=2}^{r} (z-1) \cdot (\sum_{\nu=-1}^{1} \lambda_\nu f_{i(k,j)+\nu}). \tag{16}$$

As discussed by Roe,[4] $f_{i(k,j)}$ can be obtained by the average value for all sites on the $i(k,j)$th layer. Its average value is explicitly relevant to the number of vacant sites on the $i(k,j)+\nu$ layer for $\nu = \pm 1$. Additionally, the dependence of $f_{i(k,j)+\nu}$ on the concentrations of the same and adjacent layers should be taken into account because of the anisotropic character of the concentration profile in adsorption layers. Therefore, we assume that, like Roe's method,[4] $f_{i(k,j)+\nu}$ is proportional to $\varphi_2^{i(i,j)+\nu}$. This factor is also divided by $\varphi_2^{i(k,j)}$ as the constraint of the possible placement of the preceding segment on $i(k,j)$th layer. Thus, $f_{i(k,j)+\nu}$ can be written as

$$f_{i(k,j)+\nu} = [\frac{\varphi_2^{i(k,j)+\nu}}{\varphi_2^{i(k,j)}}] \cdot [\frac{L - \epsilon_{i(k,j)+\nu}}{L}]. \tag{17}$$

where $\varepsilon_{i(k,j)+\nu}$ is the number of segments on $i(k,j)+\nu$ th layer. If we focus our attention on ith adsorption layer, $\varepsilon_{i(k,j)+\nu}$ can be replaced by ε_i, which is only used as a dummy variable upon calculating the multiple product in Ω. Thus, w_k is rearranged as follows.

$$\begin{aligned}\omega_k = [\frac{z-1}{L}]^{(r-1)} \cdot &\prod_{j=2}^{r} [\sum_{\nu=-1}^{1} \varphi_2^{i(k,j)+\nu} / \varphi_2^{i(k,j)}] \\ &\cdot \prod_{i=1}^{M} \prod_{\epsilon i=0}^{\varepsilon_{i,k-1}} \frac{(L-\epsilon_i)!}{(L-\epsilon_i-1)!}\end{aligned} \tag{18}$$

Since we consider that there are n_2^i polymer segments on the ith layer, the contributions of N_2 polymer molecules to ith adsorption layer would be equal to the amount of n_2^i/r, and the upper ranking number of ε_i becomes n_2^i-1. Thus, Ω is obtained as follows:

$$\begin{aligned}\Omega = \prod_{i=1}^{M} \frac{L!}{(n_2^i/r)! \cdot n_1^i!} \cdot [\frac{z-1}{L}]^{n_2^i(1-1/r)} \\ \cdot [\sum_{\nu=-1}^{1} \lambda_\nu \varphi_2^{i+\nu} / \varphi_2^i]^{n_2^i(1-1/r)}.\end{aligned} \tag{19}$$

Here the non-local factor (final expression in the above equation) is converged to 1 in the case of bulk solution limit when $i \to \infty$. Accordingly, the logarithm of Ω becomes

$$\begin{aligned}\ln \Omega = -L \sum_{i=1}^{M} \{\varphi_1^i \ln \varphi_1^i + (\varphi_2^i/r) \ln(\varphi_2^i/r) - (1-1/r) \varphi_2^i \\ \ln((z-1)/e) - \varphi_2^i (1-1/r) \\ \ln[\sum_{\nu=-1}^{1} \lambda_\nu \varphi_2^{i+\nu} / \varphi_2^i]\}\end{aligned} \tag{20}$$

The boundary condition in Ω at or near the interface, when applied to present ternary system having a semi-open boundary at interface, is easily obtained by the relation that, for example, the region when $\alpha(i) < 0$ belongs to β-phase. In other words, $\varphi_2^{\alpha(i)} = \varphi_2^{\beta(i)}$ when $\alpha(i) < 0$.

Bulk concentration equilibria, concentration distribution, adsorption, interfacial tension. The equilibrium bulk concentrations of the two biphasic solutions can be easily determined by the condition of equal value of the chemical potential of a polymer molecule in bulk polymer phases of two subsystems. Therefore, we have the simple relation as follows:

$$[\frac{\partial \ln Q^\alpha}{\partial n_2^{\alpha(*)}}]_{n_1^{\alpha(*)}, T, V} = [\frac{\partial \ln Q^\beta}{\partial n_2^{\beta(*)}}]_{n_1^{\beta(*)}, T, V} \tag{21}$$

Thus, from *eqns* 6-8, 20, and 21, we obtain following relation of equilibrium bulk concentrations of two biphasic solutions:

$$\begin{aligned}(1/r) \cdot \ln(\varphi_2^{\alpha(*)} / \varphi_2^{\beta(*)}) + (1-1/r) \cdot (\varphi_2^{\alpha(*)} - \varphi_2^{\beta(*)}) \\ + (\chi_\rho^\beta - \Delta\chi_\rho) \cdot (1 - \varphi_2^{\alpha(*)})^2 - \chi_\rho^{\beta(*)} (1 - \varphi_2^{\beta(*)})^2 = 0.\end{aligned} \tag{22}$$

where $\Delta\chi_\rho \equiv \chi_\rho^\beta - \chi_\rho^\alpha$.

The equilibrium concentration profile in each phase is obtained by the maximum term method used by Roe[4] as follows:

$$[\frac{\partial \ln Q^\pi}{\partial \varphi_1^{\pi(i)}}]_{i \neq j, T, V, L} = [\frac{\partial \ln Q^\pi}{\partial \varphi_1^{\pi(*)}}]_{T, V, L} \tag{23}$$

Then, the corresponding expression for the concentration profile in each of the two biphasic solutions is obtained as

$$\begin{aligned}&\ln \varphi_1^{\pi(i)} - (1/r) \cdot \ln \varphi_2^{\pi(i)} + (1-1/r) \cdot \ln[\sum_{\nu=-1}^{1} \lambda_\nu \varphi_2^{\pi(i+\nu)} / \varphi_2^{\pi(i)}] \\ &+ (1-1/r) \cdot [\sum_{\mu} \frac{\varphi_2^{\pi(i-\mu)}}{\sum_{\nu} \lambda_\nu \varphi_2^{\pi(i-\mu+\nu)}} - 1] + \chi_\sigma^\pi \cdot \delta_{\pi(1), \pi(i)} \\ &+ \chi_\rho^\pi \sum_{\nu=-1}^{1} \lambda_\nu (\varphi_2^{\pi(i)} - \varphi_1^{\pi(i)}) = \ln \varphi_1^{\pi(*)} - (1/r) \cdot \ln \varphi_2^{\pi(*)} \\ &+ \chi_\rho^\pi \cdot (\varphi_2^{\pi(*)} - \varphi_1^{\pi(*)}), \quad \text{for } \pi = \alpha, \beta,\end{aligned} \tag{24}$$

where $\chi_\sigma^\beta = \chi_o - m\chi_\rho^\alpha$, $\chi_\sigma^\alpha = \chi_o - m\chi_\rho^\beta = \chi_\sigma^\beta - m\Delta\chi_\rho$, and $\delta_{\pi(1), \pi(i)}$ is Kronecker's delta.

As a measure of extent of polymer adsorption at the interface, we adapt the usual definition of surface excess of polymer segments per surface site as follow:

$$\Gamma^\alpha = \sum_{i=1}^{M} (\varphi_2^{\alpha(i)} - \varphi_2^{\alpha(*)}), \tag{25}$$

$$\Gamma^\beta = \sum_{i=1}^{M'} (\varphi_2^{\beta(i)} - \varphi_2^{\beta(*)}). \tag{26}$$

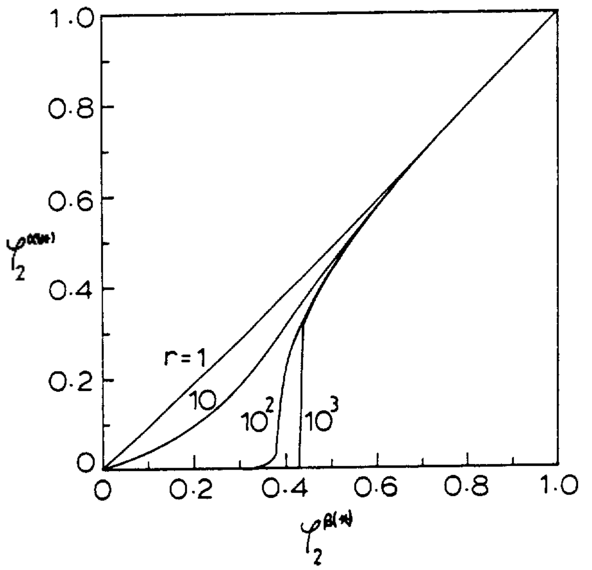

Figure 1. The bulk concentration of the polymer in α-phase $\varphi_2^{\alpha(*)}$ is plotted against $\varphi_2^{\beta(*)}$ in β-phase, for $\chi_P^\beta=0.5, \chi_\sigma^\beta=1.0, \Delta\chi_P=-0.1$. The values of degree of polymerization r are indicated. Note the abrupt increasing regions of $\varphi_2^{\alpha(*)}$ for $r=100$, 1000.

The interfacial tension of this system can be derived from the surface excess Gibbs free energy as shown by Roe[4]. The interfacial tension of β-phase is accordingly obtained as

$$\frac{r^\beta a}{kT} = \frac{(\chi_0 \varphi_1^{\beta(1)} + m\chi_P^\alpha \varphi_2^{\beta(1)})}{kT} \cdot \varphi_1^{\alpha(1)}$$
$$+ \sum_{i=1}^{M'} \{ \varphi_1^{\beta(i)} \ln(\varphi_1^{\beta(i)}/\varphi_1^{\beta(*)}) + (\varphi_2^{\beta(i)}/r) \cdot \ln(\varphi_2^{\beta(i)}/\varphi_2^{\beta(*)})$$
$$+ (1-1/r) \cdot [(\varphi_2^{\beta(i)} - \varphi_2^{\beta(*)}) - \varphi_2^{\beta(i)} \ln(\sum_\nu \lambda_\nu \varphi_2^{\beta(i+\nu)}/\varphi_2^{\beta(i)})]$$
$$+ \chi_P^\beta \cdot [\varphi_1^{\beta(i)}(\sum_\nu \lambda_\nu \varphi_2^{\beta(i+\nu)} - \varphi_2^{\beta(i)}) - \varphi_1^{\beta(*)}(\varphi_2^{\beta(i)} - \varphi_2^{\beta(*)})]\} \quad (27)$$

where $a=A/L$. The interfacial tension of α-phase can be obtained by the same manner given above.

Numerical Results and Discussion

In this section, we present some numerical results elucidating the characteristics of bulk concentration equilibria between two biphasic subsystems and the adsorption behavior, with the surface excesses Γ^α and Γ^β, concerned with the parameter set of $\varphi_2^{\beta(*)}$, r, χ_P^β, χ_σ^β and $\Delta\chi_P$. During calculation, we confine our system to an ideal flexible polymer solution system neglecting the phase separation phenomenon in poor phase and a close-packed hexagonal lattice: $\lambda_0=0.5$, $\lambda_{\pm1}=0.25$. The numerical results in this work are obtained from a successive approximation procedure as fully discussed by Roe.[4] Initially, we determine the bulk concentration of α-phase by solving *eqn* 22 according to the bulk concentration of β-phase as the reference concentration. Then, as a first approximation, we find the concentration profiles in two biphasic solutions by solving *eqn* 24 in the case that the system has an impermeable interface, and the non-local factor is equal to 1 in *eqn* 20. From the initial data, we determine the resulting concentration profile of the whole system.

Figure 1 presents the numerical results showing how the parameters of the system such as χ_P^β, χ_σ^β, $\Delta\chi_P$ and r affect the bulk concentration of α-phase against the reference one of β-phase. In this figure, at higher values of the degree of polymerization ($r=10^2, 10^3$) of the solute, there are characteristic regions in which the rapid increase of $\varphi_2^{\alpha(*)}$ against $\varphi_2^{\beta(*)}$ occurs. This phenomenon demonstrates that the solubility of the polymer in α-phase depends largely on the differential interaction energy parameter $\Delta\chi_P$ as well as the chain length of the polymer r. Below the characteristic region, the polymer molecule is unfavorable in α-phase, therefore the penetration of the polymer molecule through the interface would be allowed within only a few layers. Theoretically, the absolute

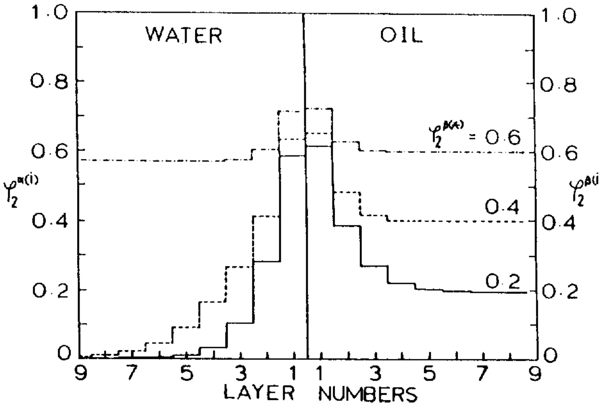

Figure 2. Segment density profiles $\varphi_2^{\alpha(i)}$ and $\varphi_2^{\beta(i)}$ as a function of the distance from the interface, for $r=1000$, $\chi_P^\beta=0.5$, $\chi_\sigma^\beta=1.0$ and $\Delta\chi_P=-0.1$. Note that each line corresponds to the whole density profile of the system obtained from the reference concentration of the polymer in bulk β-phase $\varphi_2^{\beta(*)}$ as shown.

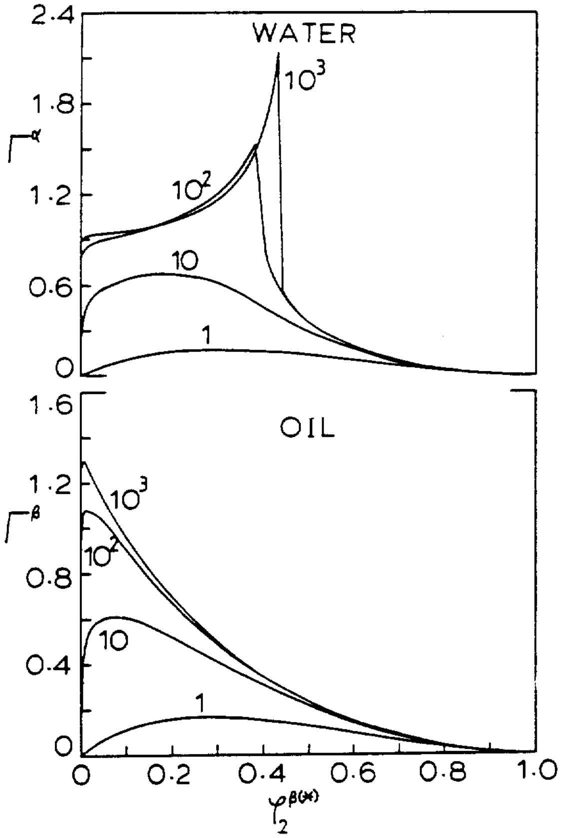

Figure 3. Surface excesses in two phase Γ^α and Γ^β are plotted against the bulk concentration of the polymer in β-phase, for $\chi_P^\beta=0.5$, $\chi_\sigma^\beta=1.0, \Delta\chi_P=-0.1$. The values of degree of polymerization r are indicated.

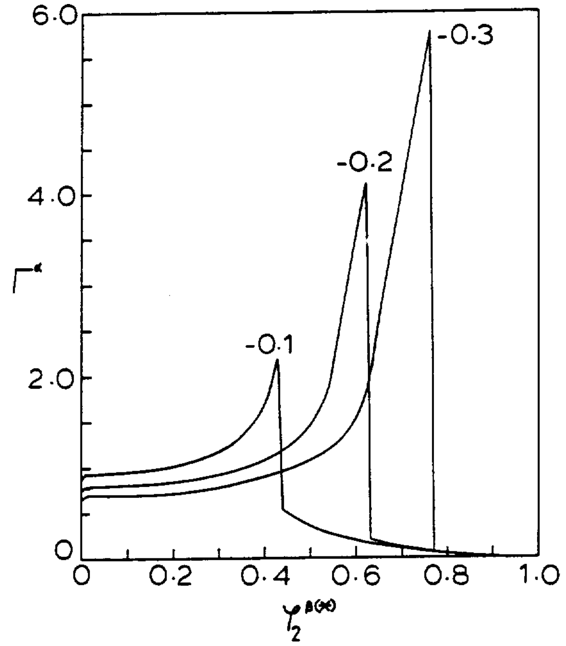

Figure 4. Surface excess in α-phase Γ^{α} is plotted against $\varphi_2^{\alpha(*)}$, for $r = 1000$, $\chi_P^{\beta} = 0.5$, $\chi_{\sigma}^{\beta} = 1.0$. The values of $\Delta\chi_P$ are indicated. The peak position is shifted to the high $\varphi_2^{\beta(*)}$ as $\Delta\chi_P$ is decreasing.

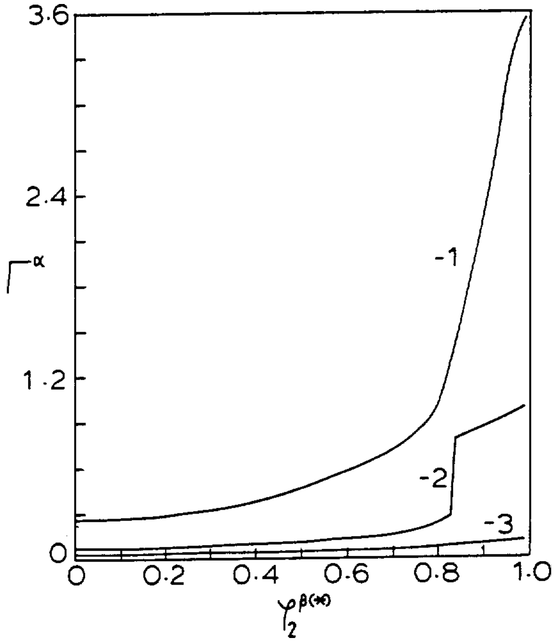

Figure 5. Similar to Figure 4, but for the large negative values of $\Delta\chi_P$. There is no peak of Γ^{α} in this case.

impermeable interface is extremely obtained when $\Delta\chi_P \rightarrow -\infty$; and $\varphi_2^{\alpha(i)} = 0$ for all i's.

In Figure 2, the typical concentration profiles of the system under consideration as a function of the distance from the interface are shown. At lower concentrations of the polymer, the segment concentration of the adsorption layer slowly converges to that of bulk phase, and the polymer concentration of α-phase is shown to be about 0. This feature of the low concentration of the polymer in β-phase demonstrates that the permeability of the polymer into the α-phase is largely restricted by its less favorability in α-phase and nearly reflected from the bulk α-phase, thus there are a few layers in α-phase where the polymer segments can be found.

Figure 3 shows the dependence of Γ^{α} and Γ^{β} on the degree of polymerization of the solute r. As shown in this feagure, the shape of Γ^{α} is similar to that of Γ^{β} at lower r. But, at higher r, there is a considerable dissimilarity between Γ^{α} and Γ^{β}. In this case, the shape of Γ^{β} is closely similar to the one in the case of adsorption at a impermeable interface. Compared with Figure 1, Γ^{α} in Figure 3 when $r = 10^3$ has a sharp peak indicating that there is a rapid increase of $\varphi_2^{\alpha(*)}$ from this point. This sharp peak of Γ^{α} may be the characteristic behavior of the polymer adsorption at a liquid-liquid interface compared with the case of the impermeable interface. Figures 4-5 show how Γ^{α} depends on $\Delta\chi_P$. In Figure 4, the peak position shifts to high $\varphi_2^{\alpha(*)}$ as $\Delta\chi_P$ is decreasing. At the peak position, Γ^{α} has a maximum value. Since the adsorption entropy is given by $\Delta S_{ad}/Lk \simeq \ln(\Omega/\Omega^{\circ})$, where Ω° corresponds to the configurational term of the normal solution limit without the interface, the maximum point of ΔS_{ad} is shown at that of Γ^{α}. In Figure 5, the case of large negative values of $\Delta\chi_P$ is demonstrated. In this case, the calculated values of $\varphi_2^{\alpha(*)}$ are less than about 10^{-100} at almost entire range of $\varphi_2^{\beta(*)}$, but the adsorption of the polymer in α-phase near the interface is apparently recognizable even when $\varphi_2^{\beta(*)}$ is small. Therefore, it may be considered that $\Delta\chi_P$ give more sensitive effect on the adsorption phenomena of the polymer at the liquid-liquid interface, and this parameter is the significant factor concerned with the stabilization of the emulsion by the polymer.

The dependence of Γ^{π} on χ_{σ}^{π} and χ_P^{π} for $\pi = \alpha, \beta$ is also a criterion of the adsorption behavior of the polymer. The detailed numerical results is not presented here, but its qualitative feature can be deduced from the full discussion of the similar aspect in the case of impermeable interface demonstrated in authors' previous work,[7] while there may be only a minor quantitative differences.

The influence of the size difference of the dissimilar solvent may give rise to the adsorption features shown previously. If we designate the thickness between the adjacent adsorption layers by d^{π} for π-phase, then, in general, it is evident that $d^{\alpha} \neq d^{\beta}$. Therefore, the lattice types of the two phases are different each other, namely, $\lambda_{\nu}^{\alpha} \neq \lambda_{\nu}^{\beta}$ for the same value of ν. But, the contribution of the difference of the lattice types between two phases to the adsorption extent may be negligible, since the numerical results are quantitatively independent of the lattice type as shown by Roe,[4] while only minor differences may occur. Furthermore, the present theory may be also applied to the adsorption phenomena at the impermeable interface. The boundary condition of the impermeable interface is simply obtained by the limiting condition that, for example, $\varphi_2^{\alpha(i)} = 0$ for all i's. As a more practical interest, our theory may be applied to the oil/water interface in the case of the unusual polymers having the polar functional groups. Since the nature of the interaction type and the conformation of a polymer chain having the polar functional groups, dissolved in water-based solution, such as hydrogen bonding and self-aggregation of the polymer chain due to the large poority of water, may be quite different from those of the ideal polymers, in order to apply our work to the adsorption of the polymer having the polar functional groups from oil/water solutions, a more detailed consideration of the interaction type and the conformation of the polymer chain in water-based polymer solution may be the essential preliminary work.

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Construction of a Dynamic Laser Light Scattering System Using a Personal Computer[†]

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A dynamic laser light scattering system has been constructed using a personal computer. The intensity of the scattered light was detected with a photomultiplier tube and a photon counter. The BCD output of the photon counter which is proportional to the intensity of scattered light is fed into a personal computer via an interface card. The personal computer was programmed as an autocorrelator in machine language. The data acquisition rate of the system was about 600 samples/s which is adequate for studies on the molecular dynamics of concentrated polymer solutions, polymer latices with large particle size, and polymer glass systems. The constructed system was tested with polystyrene latex and the measured diameter of the latex particl agrees well with the supplier's value.

Introduction

Dynamic laser light scattering techniques are now among the most frequently adopted techniques in the study of molecular dynamics in polymer solutions and melts.[1-8] Especially, the photon-counting spectroscopy (PCS) has made it possible to study the chain dynamics in polymer melts[4,5,8] for which the ordinary spectrum analysis technique suffers difficulties due to the extremely low intensities of the scattered light. The most expensive part of a commercial laser light scattering system with a digital autocorrelation capability is the digital autocorrelator. However, if a personal computer can be used in place of an autocorrelator, such a light scattering system can be constructed at a very low cost. The object of this work was to construct a low cost laser light scattering system with such a capability and with a decent data acquisition rate, then to use the instrument in researches on molecular dynamics of polymers.

Experimental

The block diagram of the overall system is shown in Figure 1. A 1.5 mW He/Ne laser (Spectra Physics, 196-1) was used as a light source. A cylindrical Pyrex vial (25 mm in diameter) was used as a sample cell, which was placed in a thermostatted brass sample holder. A photomultiplier tube (PMT, Hamamatsu, R464) in conjunction with a photon-counter (Hamamatsu, C1230) was used to detect the scattered photons. The photon-counter includes several built-in units such as a preamplifier, a discriminator, a pulse counter, and a high voltage power supply for the PMT. The PMT gives current pulses at a rate which is proportional to the intensity of the scattered light. The current pulses are amplified and discriminated by the preamplifier and the discriminator, respectively. The pulse counter counts the photon pulses from the discriminator for a given time increment and the result is available as the output in binary coded decimal (BCD) format. The BCD output of the photon-counter is read, via an interface card, into a personal computer, Apple II+compatible. An ADALAB™ Interface Card (Interactive Microwave, Inc.) was utilized to interface the computer with the photon counter. The circuit diagram and the programm-

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[†] On the occasion of sixtieth birthday of Professor Nung Min Yoon to honor his distinguished work and devotion in organic chemistry and education.

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