d up to the conformation of a chain and the geometry of a surface ensure the return of a free chain to the virtual surface, $\mathcal{W}_L = 1$. This condition holds in the upper left part of the table, which is divided by the dashed line into the regions $\mathcal{W}_L = 1$ and $\mathcal{W}_L < 1$ (the lower right part of the table).

Note that the proposed formalism is strict for Gaussian chains for any $\mathcal{W}_L \leq 1$ but is not applicable for non-Gaussian chains if $\mathcal{W}_L < 1$. In the case of expanded coils it remains approximately correct if $\mathcal{W}_L = 1$, because the density of a free coil scales as $\rho \sim N^{-4/5}$ and the reflection from an adsorbing surface in the transition point does not change the scaling law. The applicability of eq 22 and the whole scheme of definition of the transition order in adsorption to globular structures needs further analysis.

Summary

A general method for investigating the transition type during adsorption of polymer chains on various solid surfaces has been developed. It is shown that a decisive part is played by the asymptotic behavior of length distribution functions for loops formed by the return of free chains to the virtual surface geometrically equivalent to the adsorbent surface. The dependence of the chain free energy on the adsorption energy near the desorption–adsorption transition point is obtained in general form.

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Study of the Surface Tension of Polymer Solutions: Theory and Experiments. 1. Good Solvent Conditions

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ABSTRACT: A study of the surface tension of semidilute polymer solutions in good solvent conditions is presented. Theoretical predictions are given for the two cases when the interface is attractive or repulsive for the polymer, for the cases of both weak and strong adsorption. The Cahn approach for the interfacial tension is used and the concentration profile is calculated in mean field theory. The measurements were performed on two polymer good solvent systems: poly(dimethylsiloxane)–toluene and polystyrene–toluene for the attractive and repulsive cases, respectively. The well-known ring method was used. The agreement between theory and experiments is good and indicates that the two systems are strong-adsorption cases.

Recently, much effort has been devoted to the study of the interfacial properties of solutions. In particular, the behavior of polymers at liquid surfaces (melt or solution) has raised much interest, both theoretically and experimentally.

One can distinguish two different situations. The first one is the contact between two liquid phases with no discontinuity in the concentration of the constituents in the interface.[1–4] The second one concerns the presence of a wall (either at a solid–liquid or a liquid–gas interface) leading to a discontinuity of the concentrations.[5–8] We are interested in that second case since the liquid–gas surface of the solution is sharply defined.

It was observed long ago that some polymers exhibit surface activity in organic solvents. On the other hand, adsorption phenomena are frequently of great amplitude for polymer solutions in contact with surfaces.[9]

From the theoretical point of view the approach of Cahn[7] for the interfacial tension and wetting properties of fluid–solid interfaces and some recent calculations[8,10,11] of the profiles of polymer concentration in the vicinity of attractive or repulsive interfaces seem good building blocks for new predictions of interfacial behavior. This paper presents such predictions for the surface tension of semidilute solutions of polymers in good solvents. Both attractive and repulsive interfaces are examined, leading to different behaviors.

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Table I
Molecular Weights of the PDMS Samples

	polymer		
	I	II	III
$\bar{M}_n$(osmometry)	93 000	265 000	
$\bar{M}_w$(GPC)	170 000	344 000	616 000
$\bar{M}_n$(GPC)	54 000	200 000	414 000
$I_P = \bar{M}_w/\bar{M}_n$(GPC)	3.1	1.7	1.5

Much experimental data[12-14] exist in various systems and some of them were compared with different theories.[15] Unfortunately, most of these experiments were performed with low molecular weight polymers ($\bar{M}_w < 10^4$). For these molecular weights the semidilute concentration range is very narrow since the lower limit of the range (overlap concentration) varies as $M^{-0.8}$ in good solvent.

The experimental results presented here were obtained with much higher molecular weight systems ($\bar{M}_w \simeq 300\,000$) which are better candidates to test polymer theories.

I. Experimental Part

Chemicals. Two different polymers were used, polystyrene (PS) for the repulsive case and poly(dimethylsiloxane) (PDMS) for the attractive one. Toluene is a good solvent for both of them.[16,17] We used Uvasol quality toluene, purchased from Merck.

(A) Polystyrene. Two samples of polystyrene were used: one of them ($\bar{M}_w = 270\,000$, $\bar{M}_w/\bar{M}_n = 1.8$) was kindly supplied by Dr. C. Picot from the Centre de Recherches sur les Macromolécules (Strasbourg). The other one ($\bar{M}_w = 300\,000$, $\bar{M}_w/\bar{M}_n < 1.05$) was supplied by Interchim Co., France.

The measurements were made in the semidilute concentration range. In the case of $\bar{M}_w = 300\,000$, the crossover concentration corresponds to a volume fraction of 0.025.[18] All solutions were prepared by weighing polymer and solvent. The solutions were used several days after the preparation. No later change of the surface tension was observed. In order to calculate the volume fractions of the polymer in solution, we used the following values for the densities: $\rho_{PS} = 1.1$ g/cm^3 [19] and $\rho_{tol} = 0.867$ g/cm^3.[20]

(B) PDMS. The PDMS samples were prepared by anionic polymerization of hexamethylcyclotrisiloxane (D_3) under high vacuum. On adding the [221] or [211] macroheterobicyclic ligand to a benzene or toluene solution of D_3 after reaction with *n*-butyllithium at 20 °C, we obtained high molecular weight polymers after several hours at +20 °C or at −20 °C.[21-24] The living PDMS samples were terminated with trimethylchlorosilane. Polymers were recovered by precipitation in methanol and they were then dried under high vacuum. Under these conditions, the amount of cyclic byproducts is negligible. Molecular weights were measured by osmometry in toluene at 37 °C and by gel permeation chromatography in toluene at 25 °C by using a polystyrene calibration curve. The ratio $\bar{M}_w/\bar{M}_n$ was high for polymer I ($I_P = 3.1$); however, the polydispersity of PDMS was not expected to have an important influence in semidilute measurements. The results are summarized in Table I. The value for the density of PDMS in benzene is 0.998 g/cm^3.[23] We took this value for the toluene case.

Surface Tension Measurements. (A) Method. We used the well-known ring method.[25] The temperature was controlled at $T = 19.5 \pm 0.05$ °C. The apparatus was a modified Lauda tensiometer.

A platinum ring (2 cm in diameter) immersed in the polymer solution is slowly pulled toward the surface (Figure 1a). During this displacement the force exerted on the ring by the interface (and the displaced volume) is recorded. This force has a maximum value F_{max} for a certain height h_{max} of the ring (Figure 1b). When the ring is pulled beyond this value the force decreases, due to thinning of the film, leading to its rupture. If V is the volume of the solution that is drawn away by the ring at height h_{max}, the surface tension γ is given by

$$\gamma = \frac{F_{max}}{4\pi R} f(R^3/V, R/a)$$

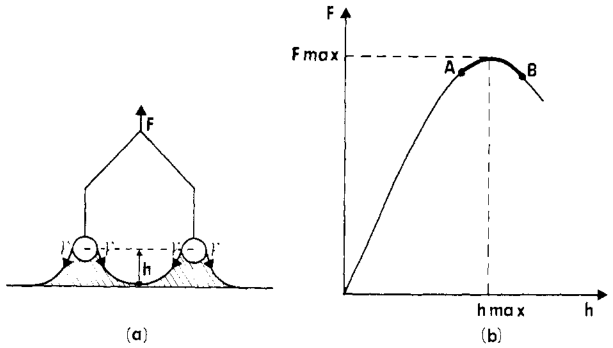

Figure 1. Schematic representation of the experimental method: (a) Vertical section of the circular ring that draws up a liquid film; the force F equilibrates the resultant of the vertical component of the tension and the weight of the film. (b) Variation of the measured force as a function of the height h. Segment AB represents the path during the oscillations.

where a is the radius of the wire constituting the ring of radius R and f is the Harkins and Jordan factor,[26] depending on the dimensionless variables R^3/V and R/a; V is calculated from F_{max} and f is obtained from curves by Harkins and Jordan.[26] To avoid border effects, the experiment is carried in a sufficiently large vessel (diameter ≥5 cm).

One problem is that during the increase of the surface due to the pull of the ring, the surface concentration must remain in equilibrium with the bulk solution. To ensure this equilibrium at height h_{max}, the ring is submitted to small oscillations around this position. The movement from A to B (Figure 1b) is slow enough to let the surface reach the equilibrium concentration. The measurement is correct when the maximum force is identical for the two displacements A → B or B → A. Nevertheless, such a procedure could not reveal a very slow approach to equilibrium (longer than several hours). For few concentrations we checked that this was not the case on a time scale of 24 h.

In previous papers, we noticed, when using the same ring method, some difficulties when the polymer solutions are concentrated. To avoid the viscoelastic surface effects occurring during the pull of the ring, we monitored the movement by a small computer: it operates by steps of 0.02-mm displacement followed by a period of rest (several minutes). This period enabled us to follow the relaxation of the viscoelastic force.

The measurement of the tension is given for each experiment within ±0.02 mN/m and the reproducibility is between 0.05 and 0.1 mN/m.

(B) Repulsive Interface (PS–Toluene). For each concentration of the solution (all of them being in the semidilute range) at least four measurements were performed. The value that we measured for toluene is $\gamma_{tol} = 28.54 \pm 0.05$ mN/m, in good agreement with tabulated values.[20]

(C) Attractive Interface (PDMS–Toluene). Several samples were used, differing in both polydispersity and molecular weight (Table I).

The measurements of the surface tension were performed on semidilute solutions. The experimental procedure was slightly different in the PDMS–toluene case due to the limited quantity of each polymer sample. In fact, the polymer solution was both stored and measured in a wide-mouth glass vessel (equipped with a stopper), the diameter of the free surface being 4.5 cm. After each measurement, toluene was added on the top of the solution. The solution was slightly stirred and left to equilibrate at least 48 h. The concentration was determined by weighing the vessel just before measurement. This procedure assures us that the surface is not overcharged in polymer. The sequence of the various concentrations was repeated two times for each sample.

II. Theory

In this section, we review the theory for the surface tension of single-phase semidilute polymer solutions. We shall consider both adsorbing (PDMS/toluene free surface) and repelling (PS/toluene free surface) interfaces with good solvent conditions. Our basic approach is to follow the Cahn[7] development for interfacial energies and wetting.

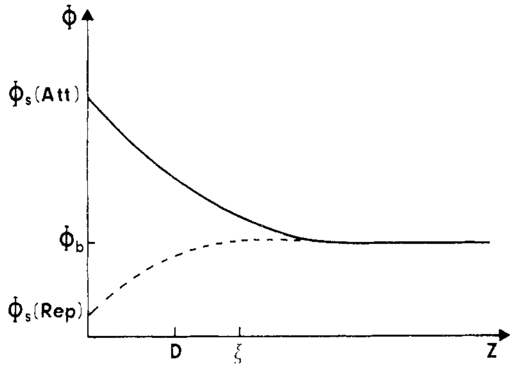

Figure 2. Sketch of the solute concentration profile in the vicinity of attractive (solid line) and repulsive (dashed line) walls.

We focus on dependences on such experimentally available parameters as polymer bulk volume fraction Φ_b, where the interfacial energy γ is written as

$$\gamma = K_1 + K_2\Phi_b^{\alpha} \qquad \text{(II.1)}$$

where K_1 and K_2 are independent of bulk polymer concentration. In order to obtain the general qualitative behavior, we shall first discuss the mean field theory for interfacial tension.[8-11] Then we will review briefly the results of another approach: indeed, in order to predict more precise exponents for the concentration dependence of the surface tension in good solvent, de Gennes[27] has applied the Widom[28] conjecture for a scaling theory of binary mixture adsorption to the case of polymer solutions; we shall show that this analysis modifies the mean field exponents in the case of attractive walls.

The Cahn[7] approach for interfacial properties of dilute solutions is based on writing the surface energy (erg/cm^2) as

$$\gamma - \gamma_0 = \gamma_l\Phi_s + \int_0^{\infty} \mathrm{d}z\, \{F(\Phi) - \mu_b\Phi + \Pi_b + L(\Phi)(\mathrm{d}\Phi/\mathrm{d}z)^2\} \qquad \text{(II.2)}$$

where γ_0 is the surface of the pure solvent, z is the perpendicular from the surface measured into the solution, $F(\Phi)$ is the bulk free energy density of a dilute solution of solute volume fraction Φ, μ_b $[=(\partial F/\partial\Phi)_b]$ is the bulk chemical potential, Π_b $(=\Phi^2[(\partial/\partial\Phi)(F/\Phi)]_b)$ is the bulk osmotic pressure, $L(\Phi)$ is a function that describes the stiffness of the solution with respect to slow spatial fluctuations of the concentration,[29] and γ_l is a local solute–interface interaction energy per unit area. Φ_s $[=\Phi(0)]$ is the solute volume fraction at the wall.

For adsorbing walls $\gamma_l < 0$, and repulsive walls leave $\gamma_l > 0$. The linear form of the concentration dependence of the local terms is always reasonable for repulsive walls but assumes weak adsorption for the attractive case. For most cases the effects of van der Waals attraction to the surfaces simply serve to renormalize the contact term γ_l.[27] This implies[30] $|\gamma_l|a^2/T < 1$. The stiffness function $L(\Phi)$ is independent of the density Φ for binary mixtures of small molecules but is strongly Φ dependent for polymers.[29] The first term on the right-hand side of II.2 represents the local contact energy between the wall and the solute; the integral term is the cost in energy associated with the deformation of the concentration profile in the vicinity of the surface (Figure 2). We now proceed to apply this Cahn surface free energy to the situations cited above.

A recent paper[15] considers interfacial tension problems within a density gradient formalism similar to that employed here and reviews the previous literature. The essential difference between that study and ours resides in the structure of the stiffness function $L(\Phi)$. For semidilute polymer solutions ($\Phi \ll 1$), $L(\Phi)$ is dominated by the configurational entropic terms rather than the spatial dependence of the monomer–monomer interactions.[31] For example, in mean field theory $L(\Phi)$ α Φ^{-1}, which when considering spatial fluctuations in bulk solutions, yields a scattering structure factor[29] of the Ornstein–Zernike form with the Edwards[32] correlation length which varies as $\Phi^{-1/2}$. In more concentrated solutions ($\Phi \lesssim 1$), we expect that $L(\Phi)$ becomes essentially Φ independent, as for binary mixtures of small molecules.[15]

(A) Mean Field Theory. In this section, we shall rederive expressions for the interfacial tension in the mean field approximation for good solvents for both repulsive[8] and attractive[10] walls using the Cahn functional (eq II.1). This enables us to make detailed comparisons with results of the de Gennes–Widom scaling theory[27,28] to be presented in the next section. Our starting point will be the Flory–Huggins free energy density for a semidilute bulk polymer solution.[29]

$$F = (T/a^3)[(\Phi/N)\ln\Phi + \tfrac{1}{2}v\Phi^2 + \tfrac{1}{6}w\Phi^3 + ...] \qquad \text{(II.3)}$$

where a is a monomer dimension and N is the degree of polymerization. The first term represents the translational entropy of a polymer chain; v and w are, respectively, the second and third virial coefficients. In good solvents $v \sim 1$ and the third virial coefficient is generally of order unity and more weakly temperature dependent than v. For semidilute polymer solutions in good solvents ($1 \gg \Phi > \Phi^*$, where Φ^* is the overlap concentration), the free energy is dominated by the effective two-body repulsions, i.e., the second virial term. For polymer solutions in mean field theory the stiffness function $L(\Phi)$ is[29]

$$L(\Phi) = (a^2/24\Phi)(T/a^3) \qquad \text{(II.4)}$$

The interfacial energy (II.2) then becomes

$$\gamma - \gamma_0 = \gamma_l\Phi_s + (T/a^3)\int_0^{\infty} \mathrm{d}z\, |\tfrac{1}{2}v(\Phi - \Phi_b)^2 + (a^2/24\Phi)(\partial\Phi/\partial z)^2| \qquad \text{(II.5)}$$

In terms of the mean field order parameter normalized to the bulk concentration, $y^2 = \Phi/\Phi_b$, the surface energy is conveniently written

$$(\gamma - \gamma_0)/\gamma_l\Phi_b = y_s^2 + \sigma_m^{-1}\int_0^{\infty} \mathrm{d}x\, |(y^2 - 1)^2 + (\partial y/\partial x)^2| \qquad \text{(II.6)}$$

where $\sigma_m = 6\gamma_l a\xi_E/T$ is a dimensionless mean field adsorption constant and lengths are measured in units of the Edwards[32] correlation length $\xi_E = a(3v\Phi_b)^{-1/2}$.

Note that the weak-coupling ($\gamma_l a^2/T < 1$) assumption is compatible with strong adsorption ($\sigma_m > 1$). The mean field profile $\Phi(z)$ is found by minimizing the free energy with variations in the profile and surface concentration Φ_s. For fixed Φ_s, the Euler–Lagrange equation derived from eq II.6 is

$$\mathrm{d}^2y/\mathrm{d}x^2 = 2y(y^2 - 1) \qquad \text{(II.7)}$$

which has a first integral

$$\mathrm{d}y/\mathrm{d}x = 1 - y^2 \qquad \text{(II.8)}$$

Note that (II.8) satisfies the boundary condition that $\mathrm{d}\Phi/\mathrm{d}x \to 0$ as $\Phi \to \Phi_b$. For attractive walls, $y > 1$ and the slope $\mathrm{d}y/\mathrm{d}x < 0$; for repulsive boundaries the inequalities are reversed.

The profiles derived from (II.8) for attractive[10,29] and repulsive[9,29] interfaces are, respectively,

$$\Phi(z)/\Phi_b = \coth^2[(z/\xi_E) + \alpha_a] \qquad \text{(II.9)}$$

$$\Phi(z)/\Phi_b = \tanh^2[(z/\xi_E) + \alpha_r] \qquad \text{(II.10)}$$

where the constants α_a and α_r are determined by the surface density Φ_s. There are two interesting limits for these profiles, depending on the arguments of the hyperbolic functions:

(i) For large arguments that correspond to either weak adsorption ($|\Phi_s/\Phi_b - 1| << 1$) or large distances ($z >> \xi_E$), the profile approaches the bulk value exponentially

$$|\Phi(z)/\Phi_b - 1| \simeq 4\exp(-2z/\xi_E) \qquad \text{(II.11)}$$

(ii) For strong adsorption ($\Phi_s << \Phi_b$ (repulsive walls) and $\Phi_s >> \Phi_b$ (attractive walls)) and in the inner region

$$\Phi(z)/\Phi_b \simeq (z/\xi_E + \alpha)^{\pm 2} \qquad \text{(II.12)}$$

where the positive exponent refers to repulsive surfaces and the negative exponent refers to attractive surfaces. The thickness D of the region where the profile is strongly deformed is

$$D/\xi_E \simeq \alpha = (\Phi_s/\Phi_b)^{\pm 1/2} < 1 \qquad \text{(II.13)}$$

Reinserting the profile into (II.6), we obtain

$$(\gamma - \gamma_0)/\gamma_1\Phi_b = y_s^2 + 2\sigma_m^{-1}\int_{y_s}^{1}(\mathrm{d}y/\mathrm{d}x)\,\mathrm{d}y \qquad \text{(II.14)}$$

The interfacial free energy is then minimized by

$$\sigma_m y_s = (\mathrm{d}y/\mathrm{d}x)_{y_s} = 1 - y_s^2 \qquad \text{(II.15)}$$

yielding

$$\Phi_s/\Phi_b = 1 + \tfrac{1}{2}\sigma_m^2 - \tfrac{1}{2}\sigma_m(\sigma_m^2 + 4)^{1/2} \qquad \text{(II.16)}$$

Recall that $\sigma > 0$ for repulsive walls and $\sigma < 0$ for attractive walls. For weak adsorption ($|\sigma_m| < 1$), the surface density is

$$\Phi_s/\Phi_b \simeq 1 - \tfrac{1}{2}\sigma_m \qquad \text{(II.17)}$$

while for strong adsorption ($|\sigma_m| > 1$)

$$\Phi_s/\Phi_b \simeq (1/\sigma_m)^{\pm 2} \qquad \text{(II.18)}$$

where the positive sign still refers to repulsive walls. More explicitly,

$$\Phi_s \simeq (12/v)(\gamma_1 a^2/T)^2 \qquad \text{(II.19)}$$

$$\Phi_s \simeq (v\Phi_b^2/12)(\gamma_1 a^2/T)^{-2} \qquad \text{(II.20)}$$

for attractive and repulsive walls, respectively. Note that for the attractive case, the surface density (in strong adsorption) is nearly independent of bulk concentration while it varies as Φ_b^2 for the repulsive situation. For weak adsorption ($|\sigma_m| < 1$), the interfacial tension is approximately linear with respect to bulk concentration

$$\gamma - \gamma_0 \simeq \gamma_1\Phi_b \qquad \text{(II.21)}$$

It is larger or smaller than the pure solvent surface tension, depending on the sign of γ_1, i.e., repulsive or attractive walls. The weak-adsorption limit is essentially a perturbation result. For the more interesting strong-adsorption limit ($|\sigma_m| > 1$), we find

$$\gamma - \gamma_0 \simeq \tfrac{2}{9}(T/a^2)(3v)^{1/2}\Phi_b^{3/2} + \mathcal{O}(\Phi_b^2) \qquad \text{(II.22)}$$

for *repulsive walls*. The leading term in $\Phi_b^{3/2}$ corresponds to the work required to create the depletion layer against the bulk osmotic pressure, i.e., $\sim\Pi_b\xi_E$. In this limit, it is essentially independent of the local surface interaction γ_1. For the *attractive case*

$$|\gamma - \gamma_0| \simeq (4\gamma_1/v)(\gamma_1 a^2/T)^2 + 2\gamma_1\Phi_b \qquad \text{(II.23)}$$

As a function of bulk concentration there is a rapid decrease in the surface tension and then a slow further linear decrease that is linear in Φ_b.

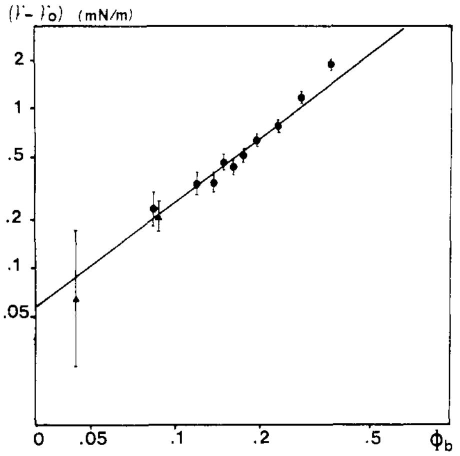

Figure 3. Repulsive case: PS–toluene. Plot of log ($\gamma - \gamma_{tol}$) as a function of log Φ_b. (▲) $\bar{M}_w$ = 300 000; (●) $\bar{M}_w$ = 270 000.

We can remark that if in the case of weak adsorption the expression of the surface tension is the same for both the attractive and repulsive cases, leading to $\gamma - \gamma_0$ linear in Φ_b, the expressions for strong adsorption are qualitatively different.

(B) Comparison with Scaling Theory. Predictions of the interfacial behavior of attractive and repulsive systems in the frame of scaling theory are given in ref 27. More detailed calculations of the profile give similar results.[33] The main conclusions for our purpose are the following: (i) the predictions for the repulsive interface are unchanged; (ii) in the attractive case, the exponent of Φ_b in the expression of γ changes from 1 to 1.25.

III. Results and Discussion

We measured the surface tension of the polymer solutions over a wide range of volume concentrations up to 0.4 in good solvent conditions. To our knowledge, only two studies refer to measurements of the surface tension of polymer solutions.[12,14] In the two systems (PDMS–toluene and PDMS–Tetralin solutions), the free surface behaves as an attractive wall. A second point is that in the two experimental studies, relatively low molecular weight (<10^4) polymers were used, which are not the best candidates to test polymer theories. Moreover, the concentration range of the semidilute regime is very limited as previously noted. The third remark is that the mean field theory gives numerical predictions that we may reasonably compare with experiments.

The theoretical predictions are related to the semidilute concentration range. In fact, the expression "semidilute range" deserves some discussion: if all the authors agree on the definition of the lower limit (overlap concentration), the upper limit is not so well understood. A good theoretical definition could be the transition from the two-body interaction (second virial coefficient in eq II.3) to higher terms of interaction. Experimentally, the situation is not very clear.[34] We consider that an upper limit of this range is 0.25.

Repulsive Interface. The measurements were done for a volume fraction of PS in toluene going from 0.04 to 0.36. The logarithmic representation of Figure 3 (log ($\gamma - \gamma_0$) as a function of log Φ_b) gives the exponent of the relation $\gamma - \gamma_0 = \beta\Phi_b^{\alpha}$. With γ_0 = 28.54 mN/m and an error of 0.05 mN/m, one gets $\alpha = 1.3 \pm 0.25$ and $\beta = 5 \pm 1$ in the semidilute range ($0.04 < \Phi_b < 0.24$).

The value of β can be deduced from the mean field theory calculations (eq II.22). If we take $v = 0.12$, using $v = 1 - 2\chi$, with χ the interaction Flory parameter ($\chi_{PS} = 0.44$[16]) and a = 3 Å, we get $\beta_{theor} = 6$. These two values

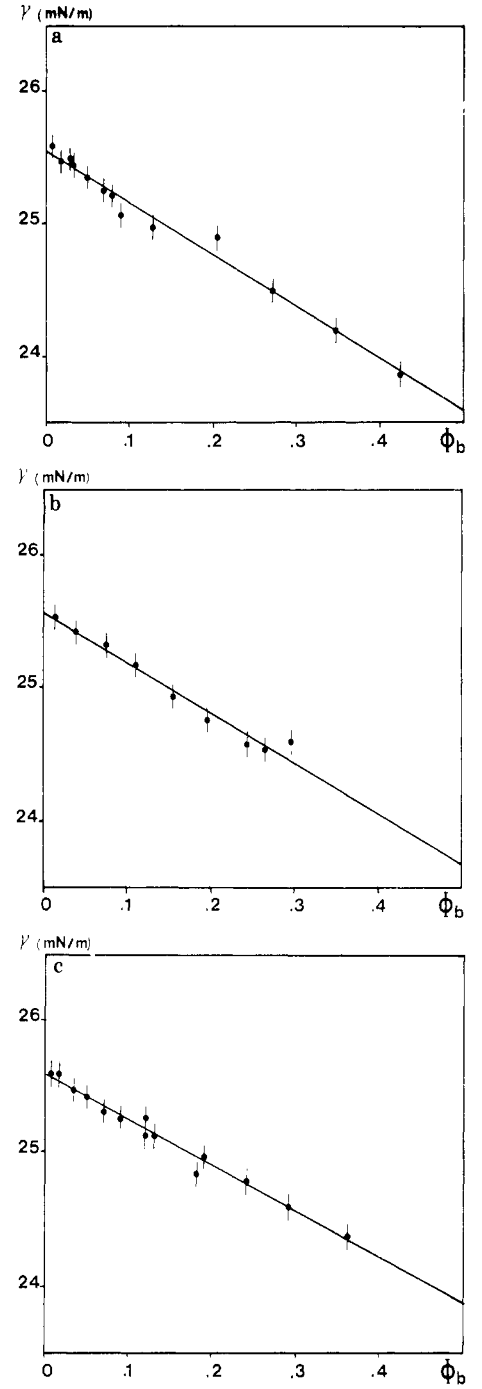

Figure 4. Attractive case: PDMS–toluene. Variation of γ as a function of Φ_b for various samples: (a) $\bar{M}_n \approx 100000$; (b) $\bar{M}_n \approx 200000$; (c) $\bar{M}_n \approx 500000$.

are in excellent agreement. It is necessary to point out that if higher concentration (>0.24) measurements are included in the fit, the exponent increases to 1.7 (concentrations up to 0.38). This could reveal a change of regime (semidilute → concentrated). As a contrary, the β term remains unchanged. We have no clear explanation of the small discrepancy between the two exponents.

Attractive Interface. Figure 4 gives the variations of γ when the volume fraction varies from 0.02 to 0.4 for three different samples.

It is interesting to compare these results with the results of ref 12 and 14. Let us recall that these authors observe for low molecular weight PDMS a progressive decrease of the surface tension γ with an increasing concentration of polymer. The highest molecular weight ($\bar{M}_n \sim 6500$) shows a sudden drop of γ (around 3 mN/m) at $c \approx 0$ followed by an almost linear decrease. Our results for molecular weights ranging from 10^5 to 5×10^5 are in agreement with these findings. The three curves of Figure 4 are well fitted with straight lines and Table II gives the parameters of the fit. ($\gamma_{ext} = \gamma(\Phi_b \rightarrow 0)$ and the slope equals $d\gamma/d\Phi_b$)

Table II

$\bar{M}_n$	γ_{ext}, mN/m	slope, m/Nm
93 000	25.55	−3.93
265 000	25.57	−3.79
500 000	25.60	−3.45

We limit our discussion to the mean field theory since the limited extension of the semidilute range to 1 decade does not enable us to distinguish between the exponents of 1 and 1.25.

It is clear from Table II that these parameters are not dependent on the molecular weight, which is expected in the semidilute regime.[35]

An important point is that the extrapolated tension at $\Phi_b = 0$ is 3 mN/m lower than the value of the surface tension of pure toluene. The comparison of eq II.21 and II.23 clearly distinguishes weak and strong adsorption cases. The PDMS–toluene system is a strong adsorption case. A more detailed comparison of eq II.23 with the experimental results γ_{ext} and $d\gamma/d\Phi_b$ enables the calculation of parameters; following $\gamma_0 - \gamma_{ext} = 4\gamma_1^3 a^4/vT^2$ and $d\gamma/d\Phi_b = -2\gamma_1$ and with $T = 4 \times 10^{-21}$ J and $v = 0.16$,[16] one can calculate $\gamma_1 = 2$ mN/m and $a = 6.7$ Å. These values are reasonable if one considers that $\gamma_{tol} - \gamma_{PDMS} \approx 8$ mN/m[13] and the monomer size (O–Si–O distance) is equal to 4 Å. These values lead to $\gamma_1 a^2/T$ (coupling constant) = 0.23 and $\sigma_{\Phi_b=0.1}$ (adsorption constant) = 6.2. These results indicate weak coupling and strong adsorption as observed.

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Registry No. Polystyrene, 9003-53-6; poly(hexamethylcyclotrisiloxane), 25084-99-5.

References and Notes

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Effect of Pressure on the Mechanical Properties of Polymers. 2. Expansivity and Compressibility Measurements

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ABSTRACT: Expansivities and compressibilities which had to be estimated in earlier work have been measured. The method by which the parameters of the free volume theory ($B, f_0, \alpha_\phi, K_\phi{}^*$, and k_ϕ) were calculated from isobaric and isothermal stress relaxation measurements has been refined. The earlier method for predicting the parameters $c_1{}^\circ$ and $c_2{}^\circ$ of the WLF equation at higher fixed pressures has been revised.

I. Introduction

Earlier work in this laboratory[1] described stress relaxation measurements under superposed hydrostatic pressure at different temperatures on selected rubberlike materials. This work led to the development of an equation predicting the superposition of the effects of time, temperature, and pressure. The equation, which will be referred to as the Fillers–Moonan–Tschoegl (or FMT) equation for convenience, is based on the free volume concept and comprises the well-known WLF equation[2] as the special case predicting the effect of temperature at constant (atmospheric) pressure.

The FMT equation takes the form

$$\log a_{T,P} = -\frac{c_1{}^{\circ\circ}[T - T_0 - \theta(P)]}{c_2{}^{\circ\circ}(P) + T - T_0 - \theta(P)} \tag{1}$$

where T and P are the (absolute) temperature and pressure, respectively, and $\theta(P)$ is given by

$$\theta(P) = c_3{}^\circ(P) \ln\left[\frac{1 + c_4{}^\circ P}{1 + c_4{}^\circ P_0}\right] - c_5{}^\circ(P) \ln\left[\frac{1 + c_6{}^\circ P}{1 + c_6{}^\circ P_0}\right] \tag{2}$$

The quantities c_1–c_6, expressed in terms of the material parameters, are

$$c_1{}^{\circ\circ} = B/2.303f_0 \tag{3.1}$$

$$c_2{}^{\circ\circ}(P) = f_0/\alpha_f(P) \tag{3.2}$$

$$c_3{}^\circ(P) = 1/k_r\alpha_f(P) \tag{3.3}$$

$$c_4{}^\circ = k_r/K_r{}^* \tag{3.4}$$

$$c_5{}^\circ(P) = 1/k_\phi\alpha_f(P) \tag{3.5}$$

$$c_6{}^\circ = k_\phi/K_\phi{}^* \tag{3.6}$$

where the first superscript on the c's refers to the reference temperature, T_0, and the second superscript refers to the reference pressure, P_0. Thus all parameters are dependent on the choice of reference temperature, $c_1{}^{\circ\circ}$ and $c_2{}^{\circ\circ}$ are dependent on the choice of reference pressure also, and $c_2{}^{\circ\circ}$, $c_3{}^\circ$, and $c_5{}^\circ$ depend, in addition, on the experimental pressure, P. Equations 3 differ from eq 40 and 41 in the earlier publication in drawing attention to these dependencies by employing the more explicit notation introduced here. Unless otherwise stated, the reference conditions are T_0 = 25 °C and P_0 = 0.1 MPa. When the temperature dependence is not expressed explicitly, the parameter is referred to the reference temperature. A material parameter referred to *zero* pressure is distinguished by an asterisk. If a parameter is referred to *atmospheric* pressure, it carries no asterisk, subscript, or superscript referring to pressure. In this way the notation is made consistent with that of the WLF equation and the symbols $c_1{}^\circ$, $c_2{}^\circ$, f_0, and α_f retain their familiar form. In most cases the numerical values of parameters referred to zero and to atmospheric pressure, respectively, differ negligibly, and so we may substitute, e.g., α_r for $\alpha_r{}^*$, etc.

In eqs 3 B is a proportionality constant well-known from the theory of the WLF equation,[1,2] f_0 is the fractional free volume at the reference temperature and reference pressure, $\alpha_f(P)$ is the thermal expansion coefficient of the free volume as a function of pressure at the reference temperature, $K_r{}^*$ is the bulk modulus of the rubber at the reference temperature and zero pressure, k_r (the Bridgman constant) expresses the pressure dependence of the modulus at the reference temperature, and $K_\phi{}^*$ and k_ϕ are the occupied volume analogues of the preceding two quantities. Of the seven material parameters appearing in eqs 3, $K_r{}^*$ and k_r can be measured independently, and they alone determine $c_4{}^\circ$. The remaining five experimental quantities, $c_1{}^{\circ\circ}$, $c_2{}^{\circ\circ}(P)$, $c_3{}^\circ(P)$, $c_5{}^\circ(P)$, and $c_6{}^\circ$, can be obtained from the empirical shift distances determined from stress relaxation measurements in the manner to be discussed below. There are thus five known quantities for five unknown ones. By contrast, measurements as a function of temperature alone (i.e., at constant pressure) lead to an underdetermined system because only two known quantities, the $c_1{}^\circ$ and $c_2{}^\circ$ parameters of the WLF equation, are available for determining the three unknowns B, f_0, and $\alpha_f = \alpha_f(P_0)$.

In the work reported in the preceding paper, $K_r{}^*$, k_r, and α_r had to be estimated or backed out from the data. We

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