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Seeking the Special Transition in Polymer Solutions: Surface Tension Measurements

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ABSTRACT: We report the first measurements of the surface tension of semidilute polymer solutions close to the critical attractive–repulsive transition and compare our results to scaling and special transition theories.

The interface of a polymer solution (volume fraction in polymer Φ_b) usually exhibits two different behaviors:[1] Attractive behavior (adsorption): polymer molecules enrich the interface ($\phi_s > \phi_b$, where ϕ_s is the surface fraction occupied by the polymer at the interface). Repulsive behavior (depletion): the interfacial region is impoverished in polymer ($\phi_s < \phi_b$). Let γ_P (γ_0) be the surface tension of the pure polymer (pure solvent). Then a very simple argument to decide on these two behaviors would be that $\gamma_P > \gamma_0$ favors depletion while $\gamma_P < \gamma_0$ favors adsorption. Naturally this argument is very crude (it ignores entropy and solvent quality) and should only be valid in the limiting cases $\gamma_P \gg \gamma_0$ or $\gamma_P \ll \gamma_0$. These two behaviors have already been studied theoretically and experimentally by surface tension measurements,[2-4] and in this paper we will focus on the $\gamma_P \simeq \gamma_0$ case to investigate the critical adsorption (special transition). The theoretical predictions are reported in the Appendix.

Surface tensions generally decrease linearly with temperature far from critical conditions (P_c, T_c) and decrease slower for pure polymer than for pure solvent. We have used this feature to choose a polymer/solvent couple that behaves as in Figure 1 and that should undergo the attractive–repulsive transition by raising the temperature. (NB We thus make the assumption that the parameter γ_1 defined in the appendix is $\simeq \gamma_P - \gamma_0$.)

Experimental Section

We have used poly(dimethylsiloxane) (PDMS). This polymeric chain is very flexible within the experimental range ($T_g \simeq -120$ °C) and so is suitable for model experiments. Three different samples have been used, and their characteristics are shown in Table I. Samples I and II have been synthesized for us by Dr. S. Boileau.[3] Surface tension measurements are large polymer consumers, and we have consequently also used a commercial polymer sold by Aldrich (secondary standard grade, sample III) which is much less viscous than samples I and II: that is why we suspect this sample to contain low-mass cyclic byproducts, on the contrary to our custom-made samples. Alkanes (that are good solvents for PDMS[5]) were spectrophotometric grade products used without further purification. The surface tension values of the different species are given in Table II.

Surface tensions have been measured by using the ring method (HBM Q11 magnetic induction transducer, HBM 3073 measure lock-in amplifier, and 2-cm-diameter platinum ring). The experimental procedure[3] is specially dedicated to polymer surface tension measurements. The main drawback of this method is that a fairly large amount of solution is needed for each measurement (at least 20 cm^3). We think that this method yields the most accurate (±0.02 dyn cm^{-1}) and reproducible (±0.05 dyn cm^{-1}) results. For each temperature (monitored within ±0.02 °C), we have successively measured the surface tension of the pure solvent γ_0 and of the polymer solution $\gamma(\Phi_b)$, $\Delta\gamma = \gamma(\Phi_b) - \gamma_0$. Density variations with temperature have been taken into account in the calculation of γ's.

Table I
Characteristics of the Polymer Samples

	sample		
	I	II	III
$\bar{M}_n$	54 000	49 000	43 900
$\bar{M}_w$	170 000		103 400
I_P	3.1		2.36

Table II
Surface Tensions of Chemicals

	γ (20 °C), dyn cm^{-1}
PDMS	$\simeq$20.5
hexane	18.46
heptane	20.26
octane	21.72
nonane	22.89

Results

Samples I and II. For these samples, which are free of low-mass cyclic byproducts, we had not enough polymer to investigate the whole concentration behavior. The results are plotted in Figure 2 and appeal for the following comments:

PDMS/hexane clearly exhibits repulsive behavior. $\Delta\gamma > 0$ and does not vary in the investigated temperature range (no δ dependence). This corresponds to a $\delta = 1$ behavior (cf. Appendix).

PDMS/octane: The 0.5% volume fraction sample should be close to the transition ($\Delta\gamma = 0$ at room temperature and increases upon heating; no sharp transition). Note the strong effect of volume fraction: the 5% clearly is an attractive case, and this may correspond to the behavior associated with $\delta = 0$ (cf. Appendix).

PDMS/nonane: This system evolves from attractive to repulsive on heating. The accuracy is not high enough to derive the α exponent of $\Delta\gamma = \delta^\alpha$ for $\phi_b \to 0$ (a rough estimate would yield $\alpha \simeq 1$ instead of 2 theoretically).

From these results we learn that the couple that should reveal the "special" behavior should be either PDMS/octane or PDMS/heptane.

Sample III. For this sample, we have checked for a 30% volume fraction solution in nonane (adsorption regime) that the detachment of the solution from the measurement ring is abrupt, thus revealing a nonelastic behavior and proving that there is no surface gelation:[6] this simple test allows us to exclude any irreversible adsorption[7] (we can also conclude that the interaction parameter is not larger than 1 in absolute units).

PDMS/hexane (Figure 3): We remark that within the accuracy of the measurements, there is no temperature effect. The results are in very good agreement with a $^3/_2$ power law as found earlier.[3] δ is of the order of +1 for this

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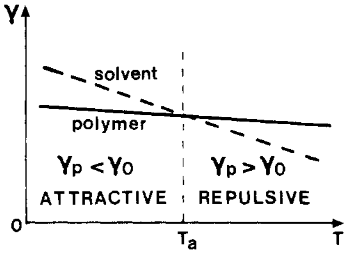

Figure 1. Differential variation of the surface tensions with temperature.

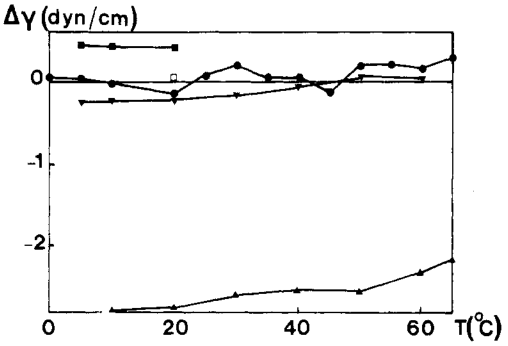

Figure 2. $\Delta\gamma$ with respect to temperature (sample I or II): (●) $\phi_b = 0.5\%$ in octane (I); (▲) $\phi_b = 5\%$ in octane (II); (▼) $\phi_b = 0.5\%$ in nonane (II); (□) $\phi_b = 5.5\%$ in heptane (I); (■) $\phi_b = 15.5\%$ in hexane (II).

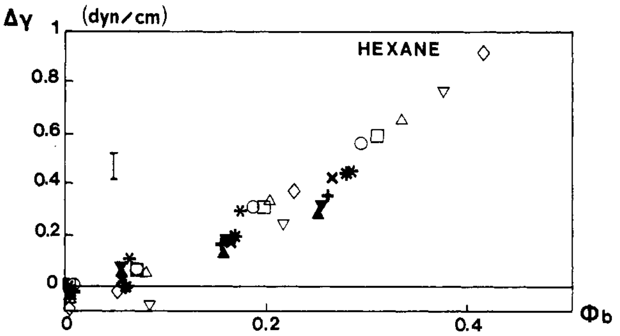

Figure 3. $\Delta\gamma$ with respect to volume fraction (solvent hexane) for different temperatures (°C) as follows: (▲) 5; (▼) 10; (+) 15; (×) 20; (✱) 25; (*) 30; (○) 35; (□) 40; (△) 45; (▽) 50; (◇) 55.

couple without any ambiguity.

PDMS/heptane (Figure 4): The surface tension now exhibits a large variation with respect to temperature, which betrays the vicinity of the transition since the concentration profiles (and thus the surface tension) are dependent in the proximal regime of δ (cf. Appendix).

PDMS/octane (Figure 5): The behavior is strictly attractive for $T > 40$ °C (there is a sharp drop of the surface tension for $\phi_b \rightarrow 0$ at low temperature), and then, upon heating, $\Delta\gamma$ apparently shows the "bumplike" behavior ($\delta \simeq 0^+$) but we do not want to emphasize this feature because of the measurement uncertainty. We can nevertheless estimate the transition temperature T_a to be equal to about 35 °C.

Discussion

Surface tension measurements are difficult, and to get a reproducibility of 0.05 dyn cm^{-1} may be already considered as satisfactory. The main problem in our experiments arises from the fact that for each temperature we had to make the *difference* of two measurements ($\gamma(\phi_b)$ and γ_0), and this naturally increases the amplitude of the error bars. One cause for the somewhat dispersed data may be due to the hydrophilic character of the PDMS: some of the measurements could have been spoiled by the presence of water. Polydispersity should not have played any role because the polymer solutions are in the semidilute regime ($\phi_b > \phi^* = N^{-4/5} \simeq 0.003$). Anyway, we can compute that at $\phi_b = 0.05$, chains with N less than 3000 are in the dilute regime: these chains will be desorbed before the long chains and will increase the surface tension before the transition of the long chains. This also may explain the "bump" for the PDMS/octane couple. We have also noticed that our custom-made PDMS were more efficient in increasing the surface tension in the depletion regime.

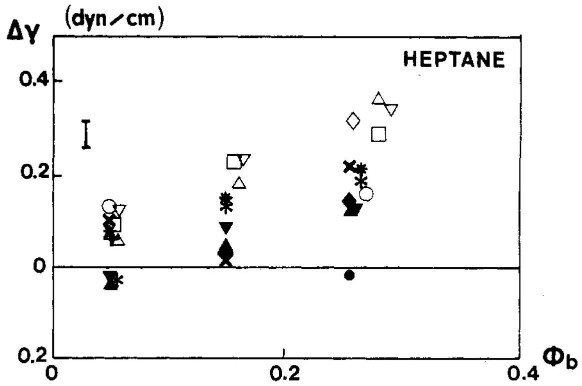

Figure 4. $\Delta\gamma$ with respect to volume fraction (solvent heptane) for different temperatures (°C) as follows: (♦) −9; (●) −5; (▲) 5; (▼) 10; (+) 15; (×) 20; (✱) 25; (*) 30; (○) 35; (□) 40; (△) 45; (△) 50; (◇) 55.

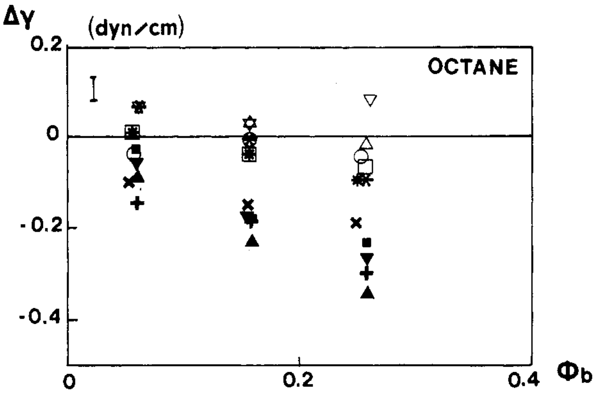

Figure 5. $\Delta\gamma$ with respect to volume fraction (solvent octane) for different temperatures (°C) as follows: (■) 1.3; (▲) 5; (▼) 10; (+) 15; (×) 20; (✱) 25; (*) 30; (○) 35; (□) 40; (△) 45; (▽) 50.

It is possible to estimate the transition temperature T_a's from the behaviors of the surface tensions with respect to temperature according to Figure 1 and following our simple argument that $\delta \propto \gamma_P - \gamma_0$. We get $T_a \simeq 0$ °C (hexane), $T_a \simeq 15$ °C (heptane), $T_a \simeq 45$ °C (octane), and $T_a \simeq 75$ °C (nonane), while we deduct from our experiments $T_a \ll 5$ °C (hexane), $T_a \simeq 0$ °C (heptane, $T_a \simeq 35$ °C (octane), and $T_a \simeq 45$ °C (nonane), which obviously is in poor agreement with the above predictions but at least shows the validity of our original assumption (the disagreement could be attributed to the fact that this assumption ignores entropy).

Conclusion

We have performed the first measurements (to our knowledge) of the surface tension of semidilute polymer solutions close to the adsorption–depletion transition. The experimental behavior is qualitatively described by the theory:

The surface tension depends strongly on the temperature around the transition (heptane, octane) while it is

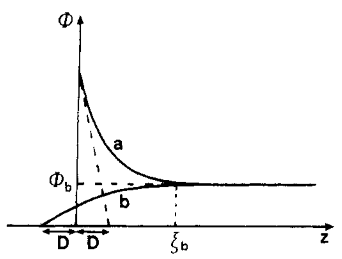

Figure 6. Theoretical profiles for $|\delta| = 1$ (after ref 2). z is the distance from the interface, and Φ_b the volume fraction.

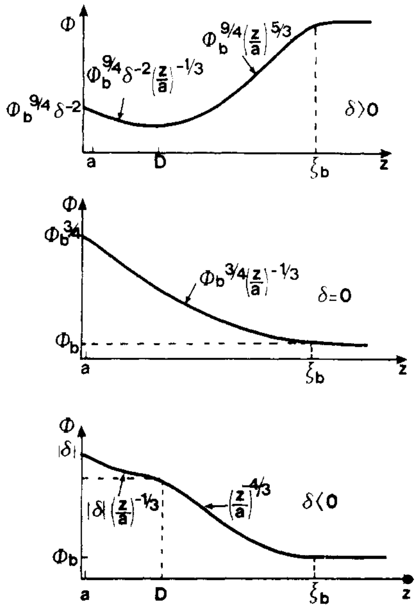

Figure 7. Theoretical profiles for $|\delta| \simeq 0$ (after ref 8).

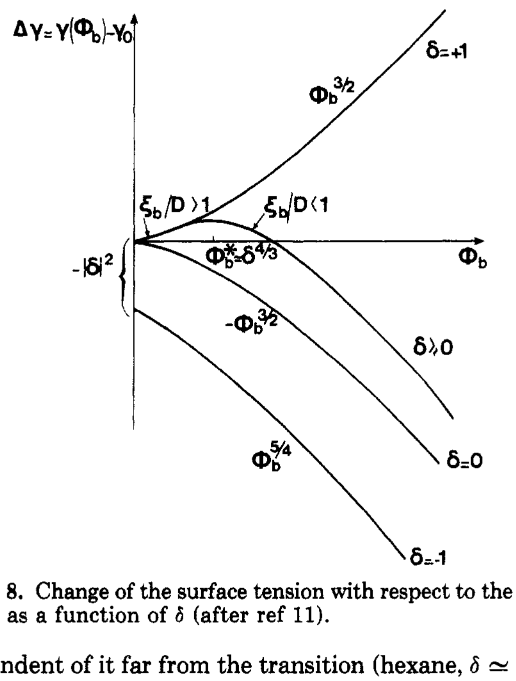

Figure 8. Change of the surface tension with respect to the pure solvent as a function of δ (after ref 11).

independent of it far from the transition (hexane, $\delta \simeq +1$). This unique feature cannot be predicted from simple scaling theory[2] or mean field theory.[3]

The sharp drop for $\phi_b \rightarrow 0$ vanishes toward the transition, and the dependence of $\Delta\gamma$ on ϕ_b is increased. The surface tension increases and then goes back to negative values around the transition (octane).

The natural prolongement of this study would be to measure the surface tension with monodisperse PDMS (prepared by successive precipitations of commercial products, for instance), but the main application of this study is to enable one to choose a polymer/solvent couple and the proper temperature range to investigate the concentration profile through structure experiments, for instance (using neutron sources[8,9]): at the critical transition the profile $\phi(z)$ should scale as $z^{-1/3}$ instead of $z^{-4/3}$ in the adsorption regime.

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Appendix

A scaling theory[2] has been developed for the interfacial behavior of semidilute polymer solutions. It distinguishes three different domains within the interfacial region (z is the distance from the interface and ξ_b the bulk correlation length $\xi_b = R_F(\Phi^*/\Phi_b)^{3/4}$ with R_F the Flory radius and Φ^* the first overlap volume fraction; Figure 6):

Proximal ($0 < z < D$): surface-sensitive region whose thickness D is defined by

$$\frac{1}{D} = \left|\frac{1}{\Phi}\left(\frac{d\phi}{dz}\right)\right|_{z=0}$$

(referred to as condition 1 in the following).

Central ($D < z < \xi_b$): self-similar polymer concentration profile.

Distal ($z > \xi_b$): the profile relaxes exponentially to $\Phi(z) = \Phi_b$. The interaction of the polymer chains with the interface is described by the parameter $\delta = \gamma_1 a^2/kT$, where $\gamma_1 a^2$ is the change in energy by the sticking to the interface of one monomer of area a^2.

Adsorption Regime ($\delta \simeq -1$). In the central domain, the unique characteristic length of the problem is z, and thus the correlation length $\xi(z)$ is proportional to z. With $\xi(z) \propto a\Phi(z)^{-3/4}$ this leads to a $\phi(z) \propto z^{-4/3}$ profile or

$$\Phi(z) = \left(\frac{a}{z + \frac{4}{3}D}\right)^{4/3}$$

to take into account condition 1. The interfacial energy W associated with the formation of the adsorbed layer of thickness D is

$$W = kT\left(\phi_s\frac{\delta}{a^2} + \frac{1}{D^2}\right)$$

The first term in parentheses is associated with the "sticking" of the polymer molecules to the wall, and the second term is an osmotic pressure term. Minimizing this expression with respect to D ($\Phi_s \propto (a/D)^{4/3}$) leads to $D = a|\delta|^{-3/2}$ ($\delta \simeq -1$ and thus $D \simeq a$). The change of interfacial tension with ϕ_b is derived from the Gibbs' relation $\Gamma = -(\partial\gamma/\partial\mu_b)$, where the surface excess Γ is defined by $\Gamma = \int_0^\infty a^{-3}(\phi(z) - \phi_b)\,dz$ and μ_b is the bulk chemical potential ($= kT/\xi_b^3$). The result is

$$\Delta\gamma = \gamma(\Phi_b) - \gamma_0 = \frac{-kT}{a^2}\left\{\left(\frac{a}{D}\right)^2 + \phi_b^{5/4}\left(\frac{a}{D}\right)^{1/3}\right\}$$

Notice the sharp drop of $\Delta\gamma$ when Φ_b goes from 0 to 0^+.

This regime may be called "weak adsorption" because the concentration profile is diffuse. Larger interaction parameters ($|\delta| > 1$) may be encountered but will lead to prewetting or surface gelation phenomena,[6] which are not described by the above theory.

Depletion Regime ($\delta \simeq +1$). The profile is assumed to obey the scaling structure $\phi(z) = \phi_b(z/\xi_b)^m$ together with condition 1. The change in interfacial tension is

$$\Delta\gamma = \frac{kT}{a^2}\left(\phi_s\frac{\delta}{a^2} + \frac{1}{{\xi_b}^3}(\xi_b - D)\right)$$

The second term is due to the creation of the depletion layer of thickness $\xi_b \simeq D$ (cf. Figure 6). Writing that this expression should be independent of the molecular mass of the polymer leads to $m = {}^5/_3$ and $D = a\delta^{-3/2}$ and finally

$$\Delta\gamma = \frac{kT}{a^2}({\phi_b}^{3/2} + {\phi_b}^{9/4}(D/a))$$

As $D \simeq a(\delta \simeq 1)$ and $\phi_b < 1$, the leading term is

$$\Delta\gamma = \frac{kT}{a^2}{\phi_b}^{3/2}$$

Special Transition. Close to the adsorption–depletion transition, $|\delta| \simeq 0$ (if T_a is the transition temperature, $\delta \propto (T - T_a)/T_a$). This case has been addressed by Eisenriegler, Kremer, and Binder[10,11] by mapping the polymer adsorption problem to the half-infinite spin problem with a short-range attractive term due to the surface. It is a multicritical problem with two associated correlation lengths: $\xi_b = (g^{-1})^{-\nu}$ ("bulk" critical length; g is the number of monomers per blob, $g = {\Phi_b}^{-5/4}$); ξ_c $(=D) = |\delta|^{-\nu/\varphi}$ ("surface" critical length), where ν is the usual exponent of critical phenomema ($\simeq$0.6) and φ is a crossover exponent. A simple physical meaning of φ can be given for a single chain: if this chain has N links, the number M of adsorbed links is $M = N^{\varphi}$. φ has been computed from scaling arguments and Monte Carlo simulations[10] and $\epsilon = 4 - d$ expansions to the second order:[12] it appears that $\varphi \simeq \nu$ (in ref 2, $\varphi \simeq 1 - \nu$). This gives now $D = a|\delta|^{-1}$. The resulting concentration profiles and surface tension[13] are given in Figures 7 and 8. The peculiar behavior associated with singular profiles can be qualitatively understood on the basis of the competition for polymers in the semidilute regime between the attraction by the wall and excluded volume effects. Notice that the first approach is a subcase of the second one for $|\delta| \rightarrow 1$ (adsorption or depletion) because then $|\delta|^{-1} = |\delta|^{-3/2} = 1$ and $D = a$.

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Dielectric Study of the Concentration Dependence of the End-to-End Distance and Normal-Mode Relaxation Time of Polyisoprene in Moderately Good Solvents

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ABSTRACT: The dielectric normal-mode process was studied for semidilute and concentrated solutions of *cis*-polyisoprene (*cis*-PI) in moderately good solvents, hexadecane (C16) and eicosene (C20). The mean-square end-to-end distance $\langle r^2 \rangle$ was determined and compared with our previous data on $\langle r^2 \rangle$ in good solvents, benzene and toluene, and those in a Θ solvent, dioxane. In dilute solutions, the values of $\langle r^2 \rangle$ in C16 and C20 were between those in the good and Θ solvents. From the expansion factor of the *cis*-PI molecules in dilute solutions, the interaction parameter χ was estimated based on the Flory theory. The double-logarithmic plot of $\langle r^2 \rangle/M$ against concentration C indicated four regimes: dilute (I), semidilute (II), semiconcentrated (II′), and concentrated (III). The C dependences of $\langle r^2 \rangle$ in regimes II and II′ were explained on the basis of the scaling theory by Daoud and Jannink and the mean-field theory by Edwards, respectively. A phase diagram classifying these regimes was obtained by plotting the crossover concentrations C^* on the solvent quality vs C diagram. The double-logarithmic plot of the relaxation time τ against C indicated that τ is independent of C in the dilute regime (I), but log τ is proportional to log C in the semidilute region (II). The dynamic crossover concentration C_τ coincided with the static crossover concentration C^* between regimes I and II.

Introduction

In our previous papers we reported that *cis*-polyisoprene (*cis*-PI) exhibits a dielectric normal-mode process due to fluctuation of the end-to-end distance.[1-3] The data of the normal-mode process provide us information on the mean-square end-to-end distance $\langle r^2 \rangle$ as well as the dynamic properties such as the relaxation time τ for the fluctuation of the end-to-end vector $\mathbf{r}$ of *cis*-PI.

Concentration C dependences of $\langle r^2 \rangle$ and τ in semidilute and concentrated solutions are recent main subjects of polymer physics.[5-11] However, τ and $\langle r^2 \rangle$ have never been measured directly by a method other than dielectric

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