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Adsorption dynamics of hydrophobically modified polymers at an air-water interface

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Abstract

The adsorption dynamics of a series of hydrophobically modified polymers, PAA_{*a*}C_{*n*}, at the air-water interface is studied by measuring the dynamic surface tension. The PAA_{*a*}C_{*n*} are composed of a poly(acrylic acid) backbone grafted with a percentage α of C8 or C12 alkyl moieties, at pH conditions where the PAA backbone is not charged.

The observed adsorption dynamics is very slow and follows a logarithmic behavior at long times indicating the building of an energy barrier which grows over time. After comparison of our experimental results to models from the literature, a new model which accounts for both the deformation of the incoming polymer coils as well as the deformation of the adsorbed pseudo-brush is described. This model enables to fit very well the experimental data. The two fitting parameters give expected values for the monomer size and for the area per adsorbed polymer chain.

Introduction

Polymers are widely used as interface stabilizers, emulsifiers or suspension dispersants. Adsorbed at the liquid/liquid or solid/liquid interfaces, polymer layers form loops, which provide a steric protection for droplets or particles against coalescence or flocculation respectively. Amphiphilic polymers, such as statistical and block copolymers or polymers grafted with hydrophobic anchors adsorb more strongly to

interfaces than homopolymers. The structure of adsorbed amphiphilic polymer layers has been the object of theoretical and experimental research in the 90s [1]. For block copolymers, it was predicted that the hydrophobic parts form 2D coils while the hydrophilic parts form 3D coils swollen in the bulk solution [2, 3]. At high surface polymer concentration, the hydrophilic parts stretch perpendicularly to the interface thus forming a pseudo-brush [1-7], the term of brush being usually reserved for covalently end-grafted polymers at a solid interface. Pseudo-brushes are also expected for other amphiphilic polymers such as telechelic [8], end-functionalized [9] or hydrophobically modified polymers [10]. The adsorption dynamics of amphiphilic polymers has attracted much less attention than their structure [11-18], even though it is relevant in foaming or emulsification processes as well as for foam and emulsion stability [19, 20]. A fine understanding of the influence of the polymer architecture on the adsorption dynamics is however required for desired applications.

Polymer molecules adsorb slowly at an interface and their surface concentration usually never reaches equilibrium [5, 10]. Millet *et al.* [10] measured a logarithmic adsorption dynamics at long time scales in the case of charged polyelectrolytes statistically grafted with hydrophobic anchors. Several theoretical studies [5, 9, 21] also predicted logarithmic adsorption regimes at long times for surfactants and polymers due to an energy barrier which grows over time. In 1952, Ward and Tordai [21] described theoretically the adsorption dynamics of surfactant molecules. They predicted an energy barrier which scales linearly with the surface pressure and the area per surfactant molecule. It corresponds to the work required to clear a section of the interface in order to allow for the adsorption of an incoming surfactant molecule. Later, Johner and Joanny [5] and Ligoure and Leibler [9] developed theories to describe the adsorption dynamics of block copolymers and of the grafting dynamics of end-functionalized polymers at an interface, respectively. In both their models, the adsorbed polymer chains form a pseudo-brush at the interface and the incoming polymer chains have to stretch and undergo a diffusive motion inside the pseudo-brush in order to reach the interface. In that case, the energy barrier arises from the stretching of the adsorbing chains but the adsorbed pseudo-brush remains undeformed. Although some attempts have been made to fit these models to experimental data [10], there is still no clear experimental validation.

In this article, we investigate the adsorption dynamics of a series of hydrophobically modified polymer molecules: PAA, poly (acrylic acid), grafted with hydrophobic alkyl anchors of varying length and grafting degree. We observe logarithmic adsorption dynamics at long times, which are compared to the models described above. We show that these models cannot satisfactorily be used to describe our data. We suggest a

new model accounting for both the deformation of the coils as they adsorb at the interface and the deformation of the pseudo-brush which has to clear a portion of the interface to enable the adsorption of a deformed coil. This new model, which involves only two fitting parameters, the area per adsorbed polymer chain and the monomer size, is in agreement with the experimental data. From the fits, we recover the expected value for the monomer size. Moreover we find that the area of an adsorbed coil is much lower than the area of an undeformed coil and does not vary significantly with the number of grafts. Our study paves the way towards the rational design of polymer molecules for interfacial stabilization.

Materials

We use a series of hydrophobically modified PAA, consisting in a PAA backbone of molar mass $M_w=100\,000$ g/mol, covalently grafted with hydrophobic alkyl chains. The PAA backbone is provided by Polysciences Inc. and the grafting reaction was done according to Wang *et al.* [22]. We refer to the grafted polymers as PAA- α -C $_n$, α being the percentage in moles of grafted monomers, and n the number of carbon atoms on the alkyl grafts. In our work, α ranges between 0.5% and 5% and $n = 8$ or 12. We keep the degree of grafting low enough to ensure a full solubility of the chains in water in acidic conditions. An illustration of the comb-like chain geometry is given in Figure 5(c).

To prepare the polymer solutions, the chains are dissolved in DI water during 60 hours. The polymer weight fraction is fixed at 1%. The pH is adjusted to pH=3 with a few milliliters of molar hydrochloric acid solution, in order to obtain conditions in which the PAA chains do not bear any negative charge. The solutions are then filtered through 0.45 μm polyvinylidene difluoride (PVDF) membranes, before being stored at 4 °C. For each experiment the solutions are kept at ambient temperature for 12 hours prior to the experiment. The solutions are used within seven days after the polymer dissolution.

Methods.

To probe the adsorption dynamics of the polymer layers, we use the pendant-drop method (Tracker apparatus, Teclis, France), which enables the measurement of the surface tension as a function of time. Details concerning the principle of this technique can be found in paper from Rotenberg *et al.* [23]. Briefly, a

fresh millimetric air bubble is formed in the polymer solution and the surface tension is then obtained as a function of time, thanks to the analysis of the bubble shape. A few milliseconds are needed to form the bubble. During this short time the polymer molecules adsorb to the interface explaining why the surface tension is not equal to surface tension of pure water with air (72 mN/m) when the measurement is started. In the following we call t_i the time at which the first surface tension measurement is made. The temperature is maintained constant at 20 °C in both the vessel and the syringe.

Results and discussion

The surface tension, γ , of the air bubble in the polymer solution is recorded as a function of time, and presented in Figure 1. The interfacial tension decreases over time, meaning that the polymer concentration at the interface, increases.

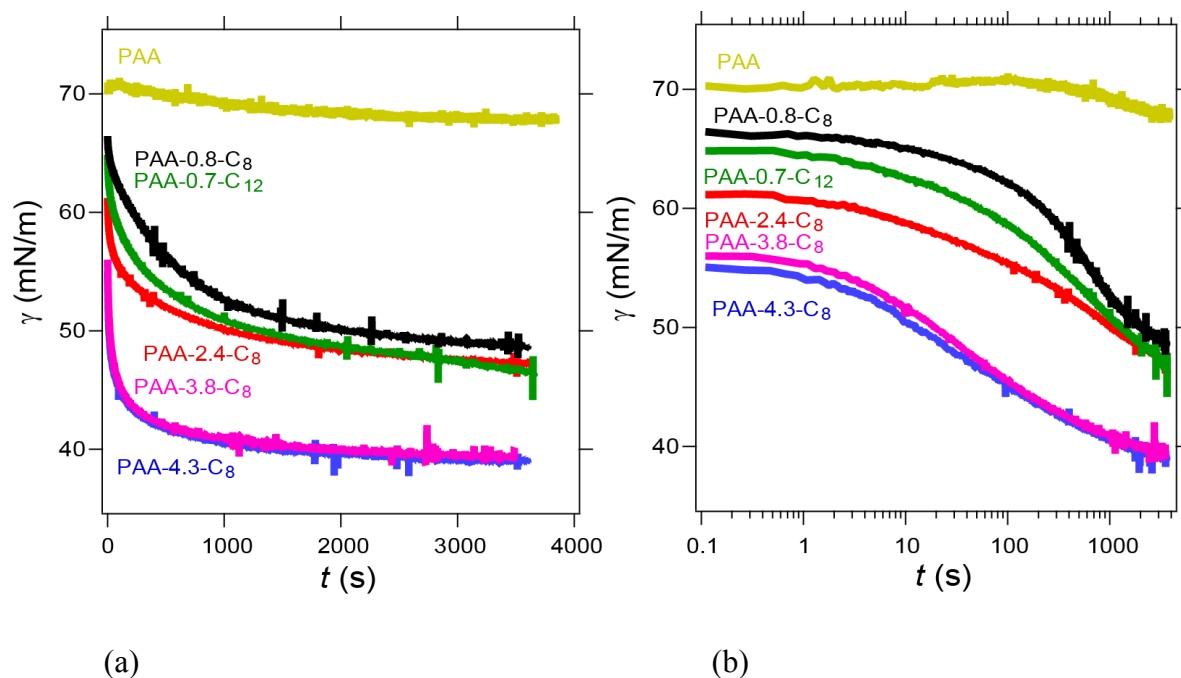


Figure 1: Air - polymer solution interfacial tension versus time during adsorption of PAA- α -C $_n$ chains on an air bubble. (a): linear scale. (b): semi-logarithmic scale.

The interfacial tension, γ , between air and a PAA solution is very close to the surface tension of water, $\gamma_0 = 72$ mN/m, which means that the adsorption of PAA chains at the interface is weak. For the grafted polymers PAA- α -C $_n$, the interfacial tension decreases faster and to a larger extent than for non-grafted PAA. We note that increasing the grafting density for a constant graft length or increasing the graft length for a constant grafting degree results in lower surface tensions. Moreover for all the grafted polymers the surface tension decreases rapidly during the first ten to hundred seconds while at longer time scales it decreases much more slowly - in a logarithmic manner. Such a logarithmic decay can be expected when the adsorption dynamics is kinetically limited by an adsorption barrier which grows over time, as predicted by several models in the literature [5, 9, 21]. In the following, our goal is to determine the origin of this barrier.

According to Benjamins *et al.* who studied the case of different proteins at the water/triacylglycerol, the chains start to deform out the interface plane when the adsorption has decreased the interfacial tension by approximately 10 mN/m compared to the pure interface [24]. For all the grafted polymers investigated, this condition is verified quickly after the formation of the interface, as evidenced by Figure 1. Moreover, using X-Ray measurements, Millet *et al.* [10] studied experimentally the same PAA- α -C $_n$ series in pH conditions where the chains are fully charged. They showed that hydrophobically modified polyelectrolytes adsorb to form a pseudo-brush, where the hydrophobic grafts stick to the interface and the charged monomer units between the grafts form stretched loops. Therefore in the following, we assume that all the grafted polymers form pseudo-brushes which become denser over time and hinder the adsorption of new incoming chains. The energy barrier may then arise *either* from the compression of the adsorbed pseudo-brush to allow for the adsorption of a new molecule *or/and* from the deformation of the incoming chains which have to stretch to penetrate into the pseudo-brush and reach the interface.

According to the Ward and Tordaï kinetic model [21], the energy barrier corresponding to the compression of an adsorbed surfactant layer to allow for a new surfactant molecule to adsorb (Figure 4(a)) simply reads

$$E_{WT} = \mathcal{A}\Pi = \mathcal{A}(\gamma_0 - \gamma) \quad (1)$$

where \mathcal{A} is the area per adsorbed molecule, Π the surface pressure, γ_0 the surface tension of pure water with air and γ the surface tension of the polymer solution with air. Far from equilibrium, the model neglects the desorption flux and the adsorption flux reads

$$\frac{d\Gamma}{dt} = k_0 C_0 e^{-\frac{\mathcal{A}\Pi}{k_B T}} \quad (2)$$

where Γ , is the number of adsorbed molecules (i.e. chains) per unit area, k_0 is a kinetic constant with the unit of a speed, C_0 the polymer concentration in the bulk solution, k_B the Boltzmann constant and T the temperature.

To integrate Equation (2) and obtain $\Pi(t)$ and $\gamma(t)$, we need a relation between the surface pressure and the surface concentration Γ . According to Aguié Béghin *et al.* [2] the surface pressure of a pseudo-brush of polymer adsorbed at an air-water interface reads

$$\Pi \approx \frac{k_B T N \Gamma}{N_B} \quad (3)$$

where N_B is the number of monomers per loop and N the total number of monomers units per polymer chain. In our case we assume that a polymer chain composed of N monomers contains αN grafts and αN loops which contain $1/\alpha$ monomers each. Therefore Equation (3) becomes

$$\Pi \approx k_B T \alpha N \Gamma. \quad (4)$$

Integrating Equation (2) and using Equation (4), we obtain the adsorption dynamics, which contains a fast adsorption regime at short times and a slower logarithmic adsorption regime at long times.

We use this model to fit our data using \mathcal{A} and k_0 as fitting parameters. The fit quality is correct (not shown). We further find that \mathcal{A} increases from 1 to 3 nm² when increasing by a factor 4 the grafting density (Figure 2), values which are all much lower than the section area of undeformed polymer coils, possibly indicating an important stretching of the adsorbed molecules. Indeed gel-permeation chromatography for PAA chains with no grafts yields an hydrodynamic radius $R_H = 10$ nm which corresponds to a section area of the order of hundreds of nm². Unfortunately, we find that k_0 increases unphysically over several orders of magnitude with the grafting density α although it is expected to be of the same order of magnitude for the different samples.

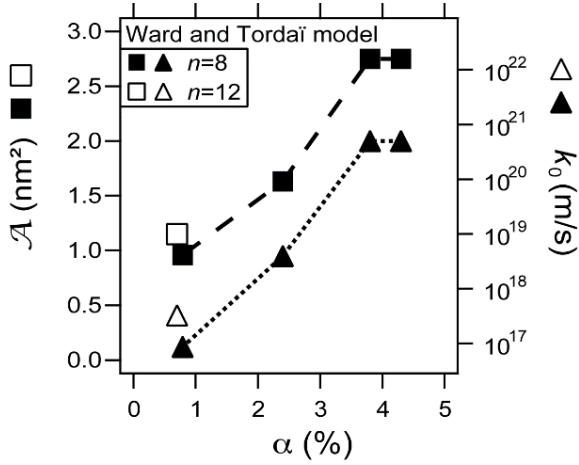


Figure 2: Values of the fitting parameters \mathcal{A} and k_0 as a function of the grafting density α using the Ward and Tordai model [21]. n the number of carbon atoms on the alkyl grafts.

This led us to investigate another model proposed by Johner and Joanny [5]. These authors consider the adsorption of amphiphilic diblocks copolymers composed of two neutral distinct blocks, one hydrophilic and one hydrophobic. In the model, the molecules form a pseudo-brush where the hydrophobic parts anchor at the interface while the hydrophilic ones extend into the solution. A logarithmic evolution of the surface coverage is predicted as the pseudo-brush sterically hinders the adsorption of incoming chains which have to stretch and diffuse by reptation through the pseudo-brush (Figure 4(b)). As the latter becomes denser, the adsorbing flux slows down, leading to a nearly-logarithmic asymptotic behavior:

$$\Gamma(t) = \frac{N_B^{-6/5}}{b^2} \left[\ln \left(\frac{t}{\tau} \right) \right]^{6/5}. \quad (5)$$

Where b is the size of a monomer and τ is a microscopic time defined by

$$\tau = \frac{6 \pi \eta}{\Phi k_B T} \quad (6)$$

with η and Φ being respectively the viscosity of the solution and the chain concentration in the bulk.

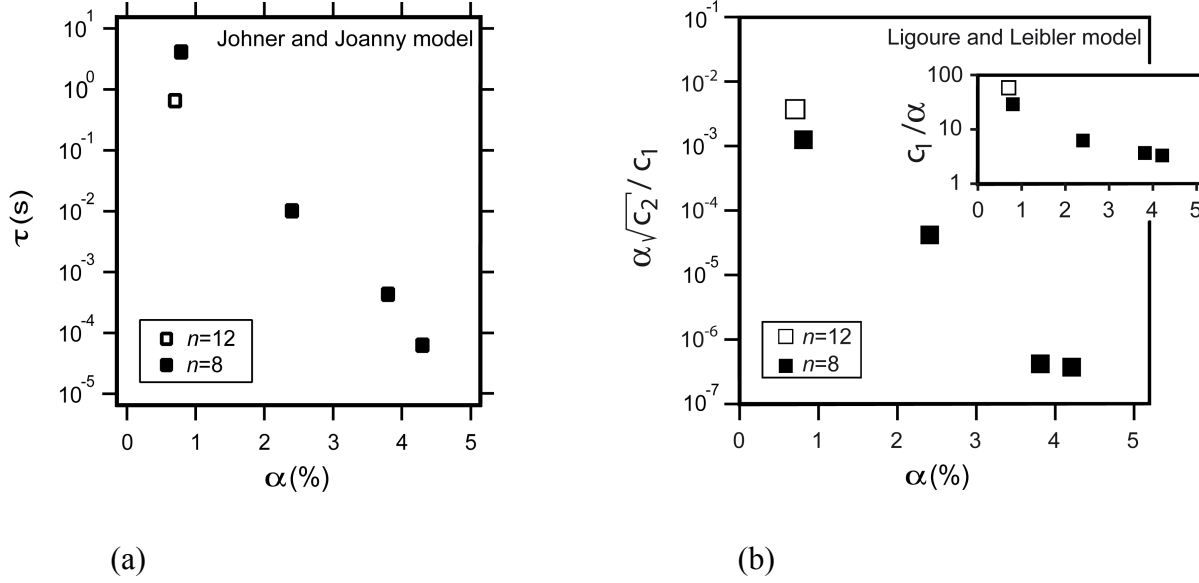


Figure 3: (a) Time constant τ as a function of the grafting density α obtained from the fitting of our experimental data to the prediction of the Johner and Joanny model (Equation (5)) [5]. (b) Combinations of the fit parameters c_1 and c_2 extracted from the Ligoure-and-Leibler model (Equation (10)) [9] as a function of the grafting degree α . n the number of carbon atoms on the alkyl grafts.

There again, the fit quality of this model with our data is correct (not shown). In Figure 3(a), we plot the parameter τ extracted from the fit of our data to Equation (5). We observe that a variation of the grafting degree by a factor 4 leads to a variation of τ over several orders of magnitude, although the latter is supposed to be constant according to Equation (6).

Another model from the literature, proposed by Ligoure and Leibler, takes the same kind of considerations into account [9]. According to this model, the surface-excess evolution is ruled by the following equation:

$$\frac{d(\Gamma/\Gamma_{\text{eq}})}{d(t/\tau_m)} = e^{-gN\Gamma^{2/3}} - \frac{\Gamma}{\Gamma_{\text{eq}}} e^{-gN\Gamma_{\text{eq}}^{2/3}} \quad (7)$$

where g is the excluded volume of the polymer chain, Γ_{eq} the surface excess at equilibrium, and τ_m a microscopic time scale. The authors argue that far from equilibrium the second term of the right-hand side of Equation (7), corresponding to the desorption flux, can be neglected, and that the evolution of Γ versus time

is very slow, justified by the experimental observation of a logarithmic-like dynamics. In these conditions, Equation (7) can be simplified and integrated, which gives:

$$\left(\frac{\Gamma}{\Gamma_{\text{eq}}}\right)^{1/3} e^{gN\Gamma^{2/3}} = \frac{2}{3} g N \Gamma_{\text{eq}}^{2/3} \frac{t}{\tau_m}. \quad (8)$$

Starting from Equation (8) (i.e. the corrected version of Equation (23) of Ligoure and Leibler [9]), one can further derive

$$\Gamma(t) = \left[\frac{1}{2gN} W\left(\left(\frac{t}{\tau_m}\right)^2 \cdot (2gN)^3 \cdot \Gamma_{\text{eq}}^2\right) \right]^{3/2} \quad (9)$$

where W is the W-Lambert function defined as follows: $y \cdot e^y = x \Leftrightarrow y = W(x)$. Finally, invoking Equations (1, 4, 9), we can fit the experimental data with the following equation:

$$\gamma(t) = \gamma_0 - c_1 \left[W\left(\frac{t^2}{c_2}\right) \right]^{3/2} \quad (10)$$

where $c_1 = \frac{k_B T \alpha}{(8g^3 N)^{1/2}}$ and $c_2 = \frac{9\tau_m^2}{(2gN)^3 \Gamma_{\text{eq}}^2}$ are the two fit parameters. We choose below to present $\frac{c_1}{\alpha}$ which only depends on the excluded volume g (at fixed T and N), and $\frac{\alpha\sqrt{c_2}}{c_1}$ which only depends on the ratio $\frac{\tau_m}{\Gamma_{\text{eq}}}$.

This model fits our data correctly (data not shown) but the parameter $\frac{\alpha\sqrt{c_2}}{c_1} \sim \frac{\tau_m}{\Gamma_{\text{eq}}}$ varies over four orders of magnitude for grafting densities α varying between 1 and 4%, as shown in Figure 3(b). These large variations of $\frac{\alpha\sqrt{c_2}}{c_1}$ are not physical. Indeed the small total variation of the surface tension (less than a factor two) measured for our different samples (Figure 1) indicates that the variations of Γ_{eq} must spread over less than an order of magnitude. Moreover, the microscopic time τ_m , defined similarly as in the Johner-and-Joanny model, should not vary by more than one order of magnitude.

The parameter $\frac{c_1}{\alpha}$ shows a more reasonable variation, as shown in the inset of Figure 3(b) but still varies by a factor larger than 10, which is unphysical for the excluded volume.

To summarize, all the models presented so far (Ward and Tordai [21], Johner and Joanny [5], Ligoure and Leibler [9]) enable us to fit our data, but in all cases, small variations of the grafting density lead to variations of the fitting parameters over several orders of magnitude. This suggests that these descriptions

overlook some contributions to the adsorption barrier. Indeed, the architecture of our polymer molecules, where the hydrophobic grafts are randomly distributed along the PAA backbone, differs notably from the one corresponding to the polymers studied by Joanny/Johner and Ligoure/Leibler and from the surfactant description of Ward and Tordai, which may explain why all these models do not describe well our data.

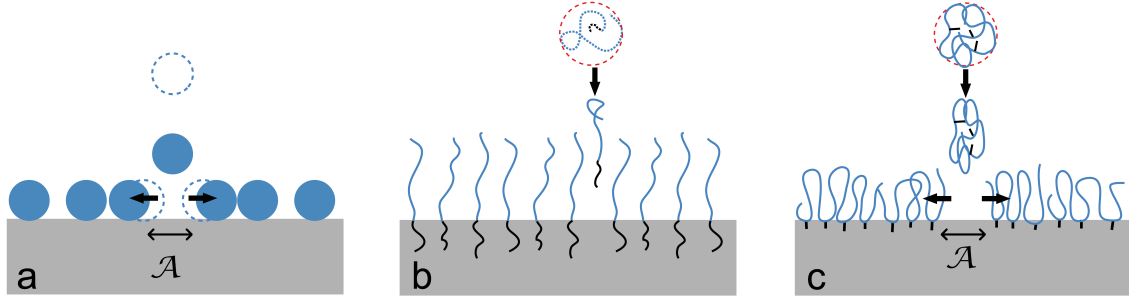


Figure 4: Schematics of different scenarios for the adsorption process. (a) Ward and Tordai model [21]: a section \mathcal{A} of the interface needs to be cleared for adsorption; (b) Johner and Joanny [5] or Ligoure and Leibler model [9]: adsorbing chains stretch before diffusing through the pseudo-brush; (c) Present model: deformation of the pseudo-brush and of the adsorbing chain.

We therefore suggest that in our case both the adsorbing polymer chains and the adsorbed pseudo-brush have to deform in order to allow for adsorption (Figure 4(c)). This new scenario would explain why the values of \mathcal{A} obtained from the Ward and Tordai fit (Figure 2) are notably smaller than the cross section of a non-deformed polymer coil. Moreover the deformation of the chains leads to an entropic barrier which adds up to the enthalpic one proposed by Ward and Tordai. To account for the entropic contribution that is not considered in the Ward and Tordai model, we propose to rewrite Equation (2) as follows

$$\frac{d\Gamma}{dt} = k'_0 C_0 e^{-\frac{\Pi\mathcal{A} + E_{\text{def}}}{k_B T}} \quad (11)$$

where E_{def} corresponds to the entropic cost for the stretching of the polymer chains and k'_0 is a kinetic constant with the unit of a speed.

The entropic cost required for a solvated chain of radius $R_F = b N^{3/5}$ (where b is the monomer size) to enter a pore of constant cross section \mathcal{A} reads [25]

$$E_{\text{def}} = \lambda k_B T \left(\frac{R_F}{d} \right)^{\frac{5}{3}} = \lambda k_B T \cdot \left(\frac{\sqrt{\pi}}{2} \right)^{\frac{5}{3}} \cdot N \cdot \left(\frac{b^2}{\mathcal{A}} \right)^{\frac{5}{6}} \quad (12)$$

where d is the pore diameter and λ a numerical prefactor of order unity that will be discussed later. We consider for now that $\lambda=1$.

The speed k'_0 is expected to be typically given by

$$k'_0 \approx \frac{R_F}{\tau_0} \quad (13)$$

where $\tau_0 \approx \frac{R_F^2}{D}$ is a microscopic diffusion time and $D = \frac{k_B T}{6\pi\eta R_F}$ the diffusion coefficient of the polymer coils diluted in a good solvent of viscosity η . Equation (13) can thus be rewritten as follows

$$k'_0 \approx \frac{k_B T}{6\pi\eta b^2 N^{6/5}}. \quad (14)$$

Injecting Equation (4) into Equation (11) leads to the following differential equation

$$\frac{d\Pi}{dt} \cdot e^{\frac{\Pi\mathcal{A}}{k_B T}} = k_B T \alpha N C_0 k'_0 e^{-\frac{E_{\text{def}}}{k_B T}} \quad (15)$$

the right-hand side of which is a constant for a given polymer, at fixed temperature and concentration in the solvent. Using Equation (1), we integrate Equation (15) between $t = t_i$ and t , which leads to

$$\gamma(t) = \gamma(t = t_i) - \frac{k_B T}{\mathcal{A}} \ln \left(1 + \frac{t - t_i}{\tau'} \right) \quad (16)$$

with t_i the time at which the first measurement is made and

$$\tau' = \frac{1}{\mathcal{A} N \alpha C_0 k'_0} e^{\frac{\mathcal{A}\Pi(t=t_i) + E_{\text{def}}}{k_B T}}. \quad (17)$$

We fit the data of Figure 1 to Equations (16) and (17) using \mathcal{A} and b as fitting parameters. As shown in Figure 5(a), we capture well the experimental dynamics with our model. We find in Figure 5(b) that the monomer size b is on the order of 1.5 Å and does not depend on α as expected. The adsorption area \mathcal{A} is of

the order of 1.5 nm^2 meaning that the chains strongly stretch (see previous discussion about Figure 2) as they adsorb at the interface. Moreover it does not vary significantly with the grafting degree. We note that we have chosen $\lambda = 1$ in Equation (12). Considering a slightly different value for λ would be equivalent to changing slightly the value of b (as $b \sim \lambda^{-3/5}$ due to the dominant exponential part). Nevertheless, b would remain independent of α and its order of magnitude would not vary.

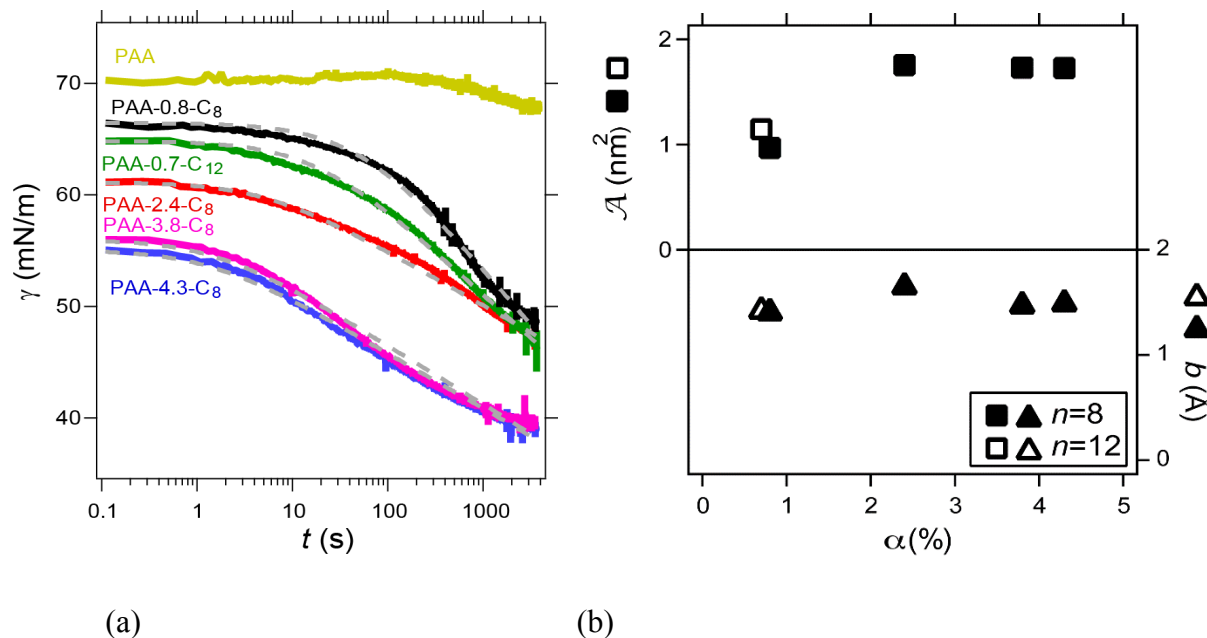


Figure 5. (a) Interfacial tensions obtained experimentally (solid lines) and from the fits using Equation (16, 17) (dashed lines). (b) Values of the parameters \mathcal{A} and b used to fit the experimental data. n the number of carbon atoms on the alkyl grafts.

Finally, we find that increasing the grafting degree enables to reach lower surface tensions at early times but does not significantly influence the adsorption kinetics. We suggest that at early times, the number of adsorbed grafts per chain increases with the degree of grafting. However at longer times, when the surface coverage becomes higher, the number of adsorbed grafts per chain saturates and becomes independent of the grafting degree.

Conclusion

In this article, using surface-tension measurements, we study the adsorption dynamics of a range of hydrophobically-grafted poly(acrylic acid), PAA- α -C $_n$, where α is the grafting degree and n the number of carbon atoms on the alkyl grafts. We measure lower surface tensions with increasing grafting degree, at early times. Moreover we find that the surface tension decreases logarithmically in time at long time scales. We compare our data with three models from the literature which predict logarithmic adsorption dynamics because of energy barriers which grow over time: the Ward and Tordai model, which predicts that the adsorption barrier scales like the area of the adsorbing molecules times the surface pressure; the Johner and Joanny model and the Ligoure and Leibler model, which both take into account the stretching of the chains as they adsorb through the pseudo-brush. We find that these models cannot be used to satisfactorily describe our data as the fit parameters extracted from them vary unphysically over several orders of magnitude. Therefore we develop a new model which takes into account both the deformation of the adsorbing polymer chains and the deformation of the adsorbed pseudo-brush. Our model, which involves only two fitting parameters, the monomer size and the area per adsorbed polymer chains, enables us to fit well our experimental data. We recover the expected value for the monomer size and we find that the adsorbed area, on the order of 1 nm², is consistent with the fact that the adsorbed polymer chains are highly compacted. Moreover we find that the adsorbed area per chain does not significantly depend on the grafting degree. The agreement of the model with the data paves the way towards a precise design of the polymer architecture in order to stabilize foams and emulsions, among other applications.

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GRAPHICAL ABSTRACT

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TITLE

Adsorption dynamics of hydrophobically modified polymers at an air-water interface

TEXT

Dynamic surface tension is used to study the adsorption dynamics of a series of hydrophobically modified polymers at the air-water interface. The adsorption dynamics is very slow and follow a logarithmic behaviors at long times, typical for an adsorption barrier that grows over time. This dynamics is well described by a model which accounts for both the deformation of the incoming polymer coils and the deformation of the adsorbed pseudo-brush at the interface.

GRAPHICAL ABSTRACT FIGURE

