Pollutant-Polysoap Interactions

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Abstract. — The influence of solubilized benzene on the viscosity of polysoaps is explained
on the basis of a simple association model for the polysoap. This model assumes aggregation of
the hydrophobic side chains into cylinders disposed along the chain backbone. Modification of
the interfacial energies of the domains by adsorption of the aromatic molecules leads to a non–
monotonic behaviour of the mean aggregate size, and a corresponding non–monotonic behaviour
of the reduced viscosity of the polysoap solutions.

Polysoaps are amphiphilic macromolecules with a comblike structure [1–5]. First designed
as water–soluble polymers [6], they have also been studied in organic solvents and have found
an increasing number of applications as liquid ion exchangers, water purifiers, enzyme models,
additives in oil recovery or emulsifiers for microemulsion polymerization of latex particles [7,8].
Polysoaps are usually depicted as polymerized surfactants, but the details of the exact config-
urations can be varied to a great extent: the position of the polar groups in the hydrophobic
side–chains; the connection to the main chain by one middle or one terminal monomer ("head"
or "tail"–polysoaps); the nature (ionic, zwitterionic) of the polar groups, which may also be
supported by the main chain; the chemical distance along the main–chain separating two side
chains; *etc.* In spite of this great variability, which has so far prevented the emergence of a uni-
fied description, many polysoaps share a few common features, recognized since the pioneering
work of Strauss in the fifties [9–14]. The most important is perhaps the absence of a critical
micellar concentration in the usual sense: micellization is here controlled by the fraction of side
hydrophobic groups along the main chain. If this fraction is large enough micelles will deco-
rate the chain even in the limits of extremely dilute polymer concentrations. Micellization can
clearly also be promoted by increasing the length of the hydrophobic side–chains or reducing
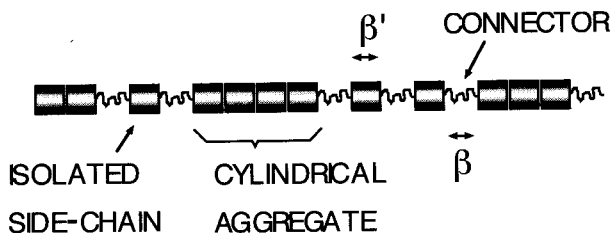the charge of the polar groups.

Fig. 1. — A model for a polysoap chain with 12 side–chains. In the cylindrical regions the connectors (not represented) are wrapped around the hydrophobic pieces. All side–chains are represented by the same area, but this does not need to be so. In fact, the model explicitly assumes that the number of available adsorption sites for the pollutant molecules in the "ones" is different from the number of available sites in each side–chain of the cylinders.

Although the formation of micelles by intra–molecular aggregation is well–established, the exact geometry of the aggregates has not yet been determined for a large number of polysoaps. However, both theory and experiments relative to the class of polysoaps that we will study below ("head"–polysoaps), seem to indicate that the hydrophobic zones have a cylindrical shape [16,17]. In a recent theoretical work Turner and Joanny [18] gave a polymer theoretical description of these molecules. These authors compared the relative stability of spherical and cylindrical micelles and concluded that cylinders are stable over a wide range of the parameters. Shih *et al.* [19] also reported evidence of cylindrical aggregation in aqueous solutions of poly(1–octadecene–*co*–(maleic anhydride)), a copolymer similar to the class of polymers studied by the Strauss group. In a recent careful study by time–resolved fluorescence quenching, Binana–Limbelé and Zana [20] concluded on the presence of polydisperse micellar aggregates in poly(disodium maleate–*co*–decylvinylether). Although the precise origin of the polydispersity is not yet determined, this observation favors the cylindrical picture for the micelles, because the cylindrical aggregates are known to be much more polydisperse than the spherical ones.

In this paper we contribute to this debate by introducing a model that describes the size variation of polysoap chains when small organic compounds are added to the polymer water solutions. The model assumes a cylindrical–like geometry for the micelles, and allows for a quantitative comparison with viscosity measurements by Layton *et al.* [11]. More generally, the model also provides a framework for discussing the influence of small adsorbate particles on the size distribution of other self–assembled cylindrical aggregates [21, 22], also known as living polymers in the context of surfactant solutions [23].

Water polysoap solutions can solubilize a large amount of small hydrophobic moieties such as benzene, heptanol or octane. In the following we will refer to these moieties as pollutants. We consider a solution of polysoaps at a given polymer concentration, and will study how aggregation of the side–chains is modified by the adsorption of the pollutants at the surface of the hydrophobic regions of the polysoaps. We consider only single–chain effects, therefore neglecting any inter–chain interaction on the adsorption mechanism. This appears to be a reasonable assumption for the system studied by Layton *et al.* [11] where the number of solubilized molecules at saturation increases linearly with the polymer content.

Our model for the polysoap chains is sketched in Figure 1. The chain is composed of three regions: single isolated side–chains, cylindrical aggregates of side–chains wrapped by the main–chain and pieces (the connectors) of the main–chain connecting the "ones" and the cylinders. Let N be the total number of side–chains in the polymer, N_1 the number of "ones" and N_L the number of cylinders containing L side–chains ($L \geq 2$). We introduce the densities $C_L = N_L/N$

($L \geq 1$) which obey the mass conservation relation

$$\sum_{L=1}^{\infty} LC_L = 1. \tag{1}$$

Given some distribution of the densities C_L the total contour length ℓ of the polysoap can be computed from

$$\ell = N \left[\beta(C_1 + \sum_{L=2}^{\infty} C_L) + \beta'(C_1 + \sum_{L=2}^{\infty} LC_L) \right] \tag{2}$$

where β is the length of a piece of main chain connecting the "ones" and the cylinders, or two different cylinders, and β' the contribution to the contour length of the polymer from each side–chain. Strictly speaking, one should choose different contour–length contributions for an isolated side–chain and for a side–chain packed into the cylinders. This would however introduce a new parameter into the problem, with very little changes to the final results. Instead of the actual length of the macromolecule, it is convenient to consider the ratio ℓ/ℓ^0, where ℓ^0 is the contour length of the polymer in pollutant–free solutions. From equations (1) and (2) one gets

$$\frac{\ell}{\ell^0} = 1 + r \frac{(C_1 - C_1^0) + \sum_{L=2}^{\infty}(C_L - C_L^0)}{1 + r(C_1^0 + \sum_{L=2}^{\infty} C_L^0)} \tag{3}$$

with the superscript " ^{0} " indicating quantities in absence of pollutant. Note that this expression carries no explicit dependence on the degree of polymerization of the polysoap, and that the two lengths β and β' only appear through the ratio $r = \beta/\beta'$.

We now calculate the density distributions C_L in the presence and in the absence of added pollutant. The free energy of the system (in units where $k_B T = 1$) is written as

$$F = C_1[\ln C_1 + E + \alpha_1 E_1] + \sum_{L=2}^{\infty} C_L[\ln C_L + E + \alpha_2 LE_2] \tag{4}$$

where the terms $\alpha_1 E_1$ and $\alpha_2 E_2$ amount for the free–energy changes induced by the pollutants on the isolated side–chains and cylinders, respectively. α_2 is the amount of moieties that can adsorb per each side–chain in cylinders and α_1 the amount that can adsorb on each unpacked side–chain. E_1 is the free energy–change per adsorption site on the "ones", and E_2 the free–energy change per adsorption site in the cylinders. In equation (4) the simple logarithmic form of the entropic contributions is valid as long as the typical aggregation number $\bar{L}_0$ of the cylinders is much smaller than N, the total number of side–groups in the polymer [18].

For pollutant–free solutions where $E_1 = E_2 = 0$ this free–energy is identical to the mean–field free energy for living–polymers [23], E being the energy penalty for creating two cylindrical end–caps. In this case minimization of (4) with respect to C_L, under the constraint (1) leads to the exponential distribution

$$C_L^0 = 4 \sinh^2\{1/(2\bar{L}_0)\}\exp\{-L/\bar{L}_0\} \simeq \frac{1}{\bar{L}_0^2}\exp\{-L/\bar{L}_0\} \tag{5}$$

where $\bar{L}_0$, which coincides with the average aggregation number in the limit $L_0 \gg 1$, varies exponentially with the end–cap energy E, $\bar{L}_0 \simeq \exp\{(E+1)/2\}$.

For polysoap solutions with pollutants one minimizes equation (4) with respect to the densities C_L, leading to

$$
\begin{aligned}
C_1 &= \exp\{-(E+1)\}\exp\{-1/\bar{L}(c)\}G(c) \\
C_L &= \exp\{-(E+1)\}\exp\{-L/\bar{L}(c)\}
\end{aligned}
\tag{6}
$$

with a partition coefficient given by $G(c) = \exp\{\alpha_2 E_2(c) - \alpha_1 E_1(c)\}$. We explicitly introduced the dependence on c, the concentration of added pollutants. By definition one has $G(c=0) = 1$ and $\bar{L}(c=0) = \bar{L}_0$. The partition coefficient $G(c)$ determines the balance between the density of "ones" and the density of cylinders. In absence of pollutants the density of "ones" is $C_1(c=0) = \exp\{-(E+1)\}\exp\{-1/\bar{L}_0\} \simeq 1/\bar{L}_0^2$. For a given concentration of added pollutants this density may be enhanced or diminished depending on the magnitude of $G(c)$. When isolated side–groups are preferred ($G(c) \gg 1$) the cylinders unwind and the total number of aggregates increase, resulting in a larger contour length for the chain. When the "ones" are energetically unfavoured ($G(c) \to 0$), they merge into the cylinders, shortening the length of the polymer. Similarly, the average aggregation number $\bar{L}(c)$ is also a function of the partition coefficient. Combining expressions (1) and (6) gives an implicit equation for $\bar{L}(c)$

$$
\frac{1}{4\,\sinh^2\{1/(2\bar{L}(c))\}} + [G(c) - 1]\exp\{-1/\bar{L}(c)\} = \frac{1}{4\,\sinh^2\{1/(2\bar{L}_0)\}}
\tag{7}
$$

which can be easily solved in the limit of large aggregation numbers $\bar{L} \gg 1$

$$
\bar{L}(c)^2 \simeq \bar{L}_0^2 + [G(c) - 1].
\tag{8}
$$

The contour length variation ℓ/ℓ^0 can also be calculated by performing the sums in equation (2) for the densities given by (5) and (6). One gets

$$
\frac{\ell}{\ell^0} = 1 + r\frac{A(\bar{L}_0)B(\bar{L}_0, G(c))}{1 + rA(\bar{L}_0)D(\bar{L}_0)}
\tag{9}
$$

with the functions A, B and D (and their asymptotic limits) given by

$$
\begin{aligned}
A(\bar{L}_0) &= \exp\{-(E+1)\} = 4\sinh^2\{1/(2\bar{L}_0)\} \simeq 1/\bar{L}_0^2 \\
D(\bar{L}_0) &= \frac{\exp\{-1/\bar{L}_0\}}{1 - \exp\{-1/\bar{L}_0\}} \simeq \bar{L}_0 \\
B(\bar{L}_0, G(c)) &= [G(c) - 1]\exp\{-1/\bar{L}(c)\} + D(\bar{L}(c)) - D(\bar{L}_0) \simeq G(c) - 1 + \bar{L}(c) - \bar{L}_0.
\end{aligned}
\tag{10}
$$

Equations (7-10) completely determine the variation of the contour–length of the polysoap chain as a function of the concentration of added pollutant. This variation depends upon r, the ratio of the contour length contributions from packed and unpacked chunks of the chain, $\bar{L}_0$ the average aggregation number in a pollutant–free solution and $G(c)$ the partition coefficient, which is still to be determined. A simple model for $G(c)$ can be provided by a Langmuir type of adsorption [4, 24] of the pollutants at the surface of the hydrophobic domains. The Langmuir scheme, that assumes random mixing of the adsorbate particles in the adsorption sites, and simple chemical equilibrium with a bulk solution at concentration c leads to

$$
E_i = -\ln(1 + \exp\{\delta_i + \mu\}) = -\ln(1 + c\,\exp\{\delta_i\}) \quad i = 1, 2.
\tag{11}
$$

In the equation above we wrote the chemical potential as $\mu = \ln c$. The adsorption parameter δ_i expresses the pollutant affinity to the hydrophobic domains. In this case the partition
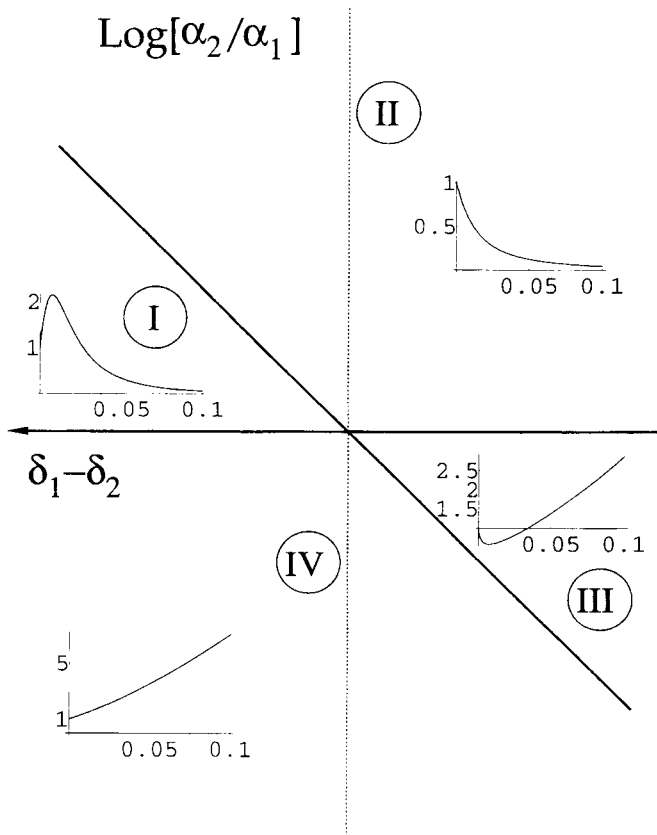
Fig. 2. — Diagram of the four possible behaviours of the partition coefficient $G(c)$. The inserts show $G(c)$ as a function of c.

coefficient can be explicitly calculated as a function of the adsorbant concentration

$$G(c) = \frac{(1 + c \exp\{\delta_1\})^{\alpha_1}}{(1 + c \exp\{\delta_2\})^{\alpha_2}} \, . \tag{12}$$

The number of adsorption sites per side–chain determines the behaviour of $G(c)$ at large concentrations. Indeed, for large c one has $G(c) \sim c^{\alpha_1 - \alpha_2}$. When there are more adsorption sites available in the isolated side–chains than in each packed side–chain ($\alpha_1 > \alpha_2$), the final structure of the chain is constituted only by single side–chains, $G(c)$ saturating at a maximum value corresponding to $C_1 = 1$. In the opposite case ($\alpha_1 < \alpha_2$), $G(c)$ tends asymptotically to zero and all the "ones" join the cylindrical aggregates. The situation for intermediate c values is more subtle, it depends on the relative values of δ_1 and δ_2. For concentrations below $\exp\{-\delta_1\}$ *and* below $\exp\{-\delta_2\}$ there are very few pollutants adsorbed onto the polymer, and $G(c)$ increases or decreases from unity depending on the sign of $(\alpha_1 \exp\{-\delta_1\} - \alpha_2 \exp\{-\delta_2\})$. This may lead to a non–monotonic behaviour. For instance, when $\alpha_2 > \alpha_1$ but $\delta_1 > \delta_2 + \log(\alpha_2/\alpha_1)$ the partition coefficient increases first for small pollutant concentrations, goes through a maximum and then decreases towards zero. Figure 2 summarizes the four possible behaviours of $G(c)$ in the phase diagram $[\log(\alpha_2/\alpha_1), \delta_1 - \delta_2]$, the average aggregation number $\bar{L}(c)$ follows also qualitatively the behaviour of $G(c)$. Note also that strictly speaking the Langmuir model

does not require adsorption *at the surface* of the hydrophobic domains, the above description also applies for absorption *inside* the domains, but the parameters α_i and E_i would then be related respectively to the number of sites available for absorption and energy of absorption.

The announced behaviour of the polysoap contour length can be directly compared to the variation of the viscosity of polysoap solutions as a function of the concentration of added pollutant. The reduced viscosity of polymer solutions is generally a power function of the length of the polymer $[\eta] \sim \ell^m$ [25]. The ratio of the reduced viscosity of a polymer solution with added pollutant $[\eta(c)]$ to the reduced viscosity of a pollutant–free solution $[\eta(c = 0)]$ is thus given by

$$\frac{[\eta(c)]}{[\eta(0)]} = \left[\frac{\ell}{\ell^0} \right]^{m+a} . \tag{13}$$

If we assume that the length increases but the chain diameter remains constant one has $a = 1$. Conversely, if the chain grows at constant volume $a = 0$. In general we expect the value of a to be between zero and one: $0 \leq a \leq 1$. The value of the exponent m, which can be determined by experiments performed in absence of pollutants, depends on the exact nature of the polymer and on the polymer concentration of the solution: rigid or flexible polymers, neutral or polyelectrolyte, dilute regime, entangled or unentangled semidilute regime.

In a series of papers [9–12] on polysoap solutions, Strauss and collaborators reported the measured viscosity of partially quaternized poly(4–vinylpyridine) with n–dodecyl bromide, in the presence of added benzene, heptanol, isooctane and n–dodecane. Two different behaviours have been observed. When isooctane or n–dodecane is added, the viscosity of the solutions is always reduced, a situation that corresponds well to the variation sketched in region II of our phase diagram (see Fig. 2). Addition of benzene or heptanol leads to a non monotonic behaviour of the reduced viscosity as a function of the pollutant concentration: the viscosity first increases, goes through a maximum and then decreases, leveling out at a value smaller than the viscosity of the non–polluted solution. This behaviour corresponds to the situation despicted in region I of the phase diagram. Our model allows not only to a qualitative comparison with experiments but it can be brought into close agreement with the actual data. As an example we compare in Figure 3 our prediction in equation (13) to the experimental points of curve 3, presented in Figure 1 of reference [11]. The simple Langmuir model presented above for adsorption fits well the data, with a reasonable set of parameters (see Fig. 3). Even with such a high number of parameters the fitting procedure is stable, due to the constraints that different parts of the curve impose on different parameters. L and m have the smallest accuracy ($\sim 30\%$). Other curves in Figure 1 of reference [11] can also be fitted by a different set of parameters. Thus interchain interactions are to some extent accounted for by our model. In fact, we assume that these interactions, which are clearly dependent on the polymer concentration, effectively change the value of the parameters of our model, but do not lead to interchain association. In the experiments of reference [11] such mechanism is supported by the fact that the number of pollutant molecules needed to bring the viscosity to its maximum varies linearly with polymer concentration. If the increase in viscosity was due to the formation of interchain aggregates, one would rather expect a variation of that number with at least the square of the concentration. However we should remark that intrachain association involving side–groups from well–separated regions of the same chain would be compatible with that linear variation. This would not modify substantially our aggregation model but could affect the exponent m in equation (13).

The structure of the partition coefficient of equation (12) corresponds to a simple, tractable model for the interactions, that can be rationalized as follows. We suppose that the aggregation process is most likely to induce changes in the conformations of the side–chains. The packed

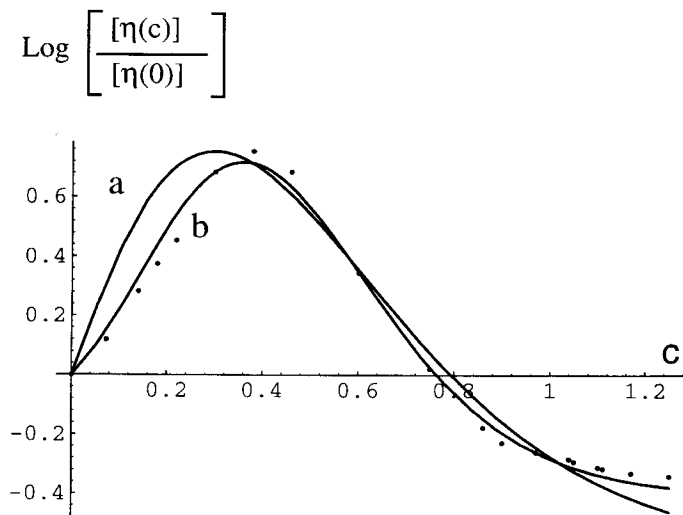$$\text{Log}\left[\frac{[\eta(c)]}{[\eta(0)]}\right]$$

Fig. 3. — Dots: the variation of the reduced viscosity as a function of the added benzene concentration (in g/100 ml) in an aqueous solution of 2 g/100 ml of partially quaternized poly(4–vinylpyridine) with n–dodecyl bromide [11]. a) The prediction of equation (13) for the Langmuir adsorption with: $m + a = 4$, $L_0 = 3$, $\delta_1 - \delta_2 = 1.38$, $r = 5$, $\alpha_1 = 10$, $\alpha_2 = 27$. b) The prediction of equation (13) for the Ising-like adsorption with: $m + a = 4$, $L_0 = 3.8$, $\delta_1 - \delta_2 = 1.23$, $w = 0.3$, $r = 4$, $\alpha_1 = 10$, $\alpha_2 = 27$.

and unpacked side–chains will thus not only have different surface to volume ratios that will translate into different numbers of possible adsorption sites, but will also present different effective surfaces to the solvent, resulting in different adsorption energies per site. By keeping the description of the pollutant/polysoap interactions at this level we certainly ignore many microscopic details such as the contributions from the polar heads or from the main chain wrapped around the cylinders, the non–uniformity of the distribution of possible adsorption sites, the solvent penetration into the hydrophobic zones, the local rigidity of the chains... However, the model can be easily extended in order to account for other phenomena that might play a role in adsorption. For instance it may be necessary to account for the mutual interactions of the hydrophobic molecules on the surface. The adsorption of benzene could in fact be a cooperative phenomenon, the adsorption of one molecule reducing or enhancing the probability of adsorption of another molecule in the neighborhood of the first one. Cooperativity can be accounted for by the Ising model extended to lattice–gas systems [26, 27]. In one–dimension there is an exact expression for the free–energy changes induced by adsorption:

$$E = -\ln\left(\frac{b+1}{b+1-2\rho}\right) \tag{14}$$

$$b = \frac{e^{w/2}\cosh H}{\left[e^{-w} + e^{w}\sinh^2 H\right]^{1/2}} \tag{15}$$

$$1 - 2\rho = \frac{e^{w/2}\sinh H}{\left[e^{-w} + e^{w}\sinh^2 H\right]^{1/2}} \tag{16}$$

with $2H = -\ln\{c\exp\{\delta + 2w\}\}$. As before c is the pollutant concentration and δ the energy

gained by an adsorbed pollutant molecule. The parameter w is the excluded volume between two adsorbed molecules. In order to induce some attraction between adsorbant pollutants one needs to have negative w values, a positive w implies repulsion between the molecules. The particular case of $w = 0$ corresponds to the Langmuir equation (11). The parameters α_1 and α_2 govern as before the behavior of $G(c)$ (and thus of ℓ/ℓ^0) at large concentrations: $\ell/\ell^0 > 1$ if $\alpha_1 > \alpha_2$ and $\ell/\ell^0 < 1$ if $\alpha_1 < \alpha_2$. Considering cooperativity improves somewhat the fitting of the viscosity curves of the experiments of Layton *et al.* as it can be seen from Figure 3 (the fit is improved by considering repulsion), but more generally the behaviour of ℓ/ℓ^0 at low concentrations follows also qualitatively the Langmuir case, increasing or decreasing according to the relative values of δ_1 and δ_2 (see diagram in Fig. 2). The effect of a negative excluded volume parameter w is important at intermediate concentrations and it can lead to the presence of a relative minimum in the viscosity curves. It is worth mentioning that such a minimum is generally observed in related self–assembled systems where adsorption of a "pollutant" plays an important role: n–dodecyl bromide compounds of poly–2–vinylpyridine and heptanol, sodium oleate and benzol [28] or sodium stearate (or palmitate) and cresol [29]. Study of the relevance of our method to explain the viscosity variation in these systems is currently under way.

In conclusion we presented a model that explains the influence of solubilized pollutants on the viscosity of polysoap solutions. The model is based on a simple model for the aggregation of the polysoap side–chains. The adsorption of pollutants at the surface of the hydrophobic cylindrical domains modifies the equilibrium aggregation size–distribution of the cylindrical domains packed along the chain backbone. This modification induces a variation of the contour length of the chain and, as a consequence, a variation of the solution viscosity. We showed that our predictions quantitatively describe experiments by Layton *et al.* The model allows also for a classification of different observed behaviours of the viscosity of polysoap solutions and other self–assembled systems, as a function of the concentration of pollutant molecules. Although we explicitly assumed a cylindrical association, the general phenomena presented here is expected to hold even for spherical aggregates. An important extension of this work would be to include non–local intrachain association, along the lines of Borisov and Halperin work [30], an effect that is likely to be important in more flexible, less charged polysoaps.

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