Self-organization of polyurethane pre-polymers as studied by self-consistent field theory

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Self-Organization of Polyurethane Pre-Polymers as Studied by Self-Consistent Field Theory

Feng Li,* Remco Tuinier,* Ilse van Casteren, Ronald Tennebroek, Ad Overbeek, Frans A. M. Leermakers

Using self-consistent field (SCF) theory, we studied the self-assembly characteristics of polyurethane pre-polymer dispersions in aqueous solutions. With a molecularly detailed model implementing the Scheutjens–Fleer discretization scheme, it is shown how the stability, equilibrium size, and internal structure of the (swollen) micelles in polyurethane (PU) dispersions depend on the chemical structure and the molecular composition of the charged pre-polymer mixtures. The stability region of these micelles is found to increase when acid groups become deprotonated and when the ionic strength is lowered. Insight into the physical–chemical behavior of PU pre-polymer dispersions is important for the subsequent process of film formation from the PU dispersions for the final coating properties.

1. Introduction

Waterborne polyurethanes (WPUs) are versatile environmentally friendly materials that are increasingly being used in coatings and adhesives for wood and automobiles as well as for numerous flexible substrates, such as textiles, leather, paper, and rubber.[1] In most applications, the final coating characteristics (including hardness, gloss) of WPUs are heavily influenced by polymer chemistry and composition. In aqueous systems, polyurethanes are not molecularly dissolved but they self- and co-assemble into colloidal particles with a typical size between 10 and

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*Supporting Information is available from the Wiley Online Library or from the author
200 nm.\textsuperscript{2} The nature, size, and stability of the resulting polyurethane particle dispersions will affect film formation and final coating properties. Understanding the behavior of the polymer dispersions will open up routes to modify and further improve the quality of WPUs products.

WPUs are synthesized via the pre-polymer mixing process (a step growth polymerization process), and PU pre-polymers were synthesized from isophorone diisocyanate (IPDI), linear hydroxyl functional polyether (polyol), and dimethylol propionic acid (DMPA) before being dispersed into water.\textsuperscript{3–6} In a pre-polymer mixing process, a low molar mass pre-polymer, composed of IPDI, a low molar mass polyol block and DMPA groups, is synthesized without addition of solvent. In general, the pre-polymers are random co-oligomers in which the ratio of the relative amounts of IPDI, polyol, and DMPA can be varied. A typical pre-polymers mixture consists of several components, some of which are amphiphilic.\textsuperscript{3} The majority of the acid groups on the pre-polymers are deprotonated by raising the pH above 7 and are subsequently dispersed in water. The (short chain) polyurethanes in these particles are subsequently chain-extended to high molar mass polyurethanes.

In this paper, the focus is on the physical–chemical properties of the pre-polymer dispersions using self-consistent field (SCF) theory. Chain extension of polyurethane pre-polymers, e.g., the reaction of isocyanate group with water, is not included in this work. In practice, these pre-polymer mixtures are complex and contain many different chemical composition distributions. It becomes very hard (maybe impossible) to predict the polymer chain sequence after chain extension of pre-polymers. In order to gain more insight, it is noted that we need to simplify the current pre-polymer mixture by focusing on the major components in this mixture discarding the ones that are present only as a minority. Some of the building block sequences in the pre-polymer mixtures may be recognized as being amphiphilic pre-polymers or “surfactant.” Figure 1 shows an example used in this study as amphiphilic polymer to stabilize the dispersed PU particles. The DMPA groups are hydrophilic (when charged), while the polyol and especially the IPDI groups are hydrophobic. We include both amphiphilic and hydrophobic (e.g., contains only IPDI and polyol fragments) pre-polymers in our model. Probably, not all pre-polymers of the real PU particles are accounted for in our study. We do, however, account for the most representative pre-polymers and those present in large quantities (under this experimental condition, see supporting information). Sequences of all the representative pre-polymers are shown in the Section 3. Amphiphilic polymers in selective solvents are known to self-assemble\textsuperscript{7} into various geometries ranging, e.g., from vesicles,\textsuperscript{8,9} disk-shaped vesicle,\textsuperscript{10} rods,\textsuperscript{11} small disks,\textsuperscript{12} to micelles.\textsuperscript{13,14} Self-organized structure from binary amphiphiles mixtures was studied both experimentally and theoretically.\textsuperscript{8,15} In comparison to those studies, a dispersion of polyurethane pre-polymers is a more complex system in the sense that these PU particles are the outcome of co-assembled multiple hydrophobic, hydrophilic, and amphiphilic polymers. To have clear distinction between these complex structures with the single component micelle, we refer them as (swollen) micelles. These pre-polymers differ in solubility by chemical structure, which makes it a challenge to study the resulting micellar structures. No systematic theoretical studies that focused on (swollen) micelle formation in significantly complex multicomponent mixture, as representative for polyurethane pre-polymer solutions, are known to us.

As theoretical method, self-consistent field (SCF) theory is used here to study the micellar structures (swollen with educts) that are being formed at polymer concentrations above the micellization threshold. SCF theory is a suitable, fast, and accurate method for studying self- and co-assembling systems. For example, it allows to predict the thermodynamic stability and structure of micelles. In micelles, the molecules typically pack densely and in order to allow the theory to be predictive, it is necessary that the size and shape of the molecules are reasonably accurately accounted for. Here, the major building block sequences of the pre-polymers are modeled in a close-to atomistic (united atoms) level. On top of this, the interactions by which the molecules interact with each other and with water need to be accounted for. In this study, we take both short-range solvency interactions as well as longer ranged electrostatic interaction into account. As a result, insight can be obtained into equilibrium micellar architectures. On top of this, the spatial distribution of pre-polymer chains in (swollen) micelles can be evaluated at the molecular level. Importantly, the modeling provides insight into the relation between pre-polymer chemistry and particle characteristics, such as size and internal compositions, and how pH and ionic strength modulate this. Again, it is stressed that we will exclusively focus on the pre-polymer mixtures and the experimental system is mimicked in a somewhat simplified version.

![Figure 1. Chemical structure of IPDI-polyol-IPDI-(DMPA-IPDI)$_2$ pre-polymer and its related coarse grained sequence used in this SCF calculation. The polyol block contains 13 repeating units.](image-url)
2. Theory for Co- and Self-Assembly

2.1. Self-Assembly of Simple and Complex Amphiphiles

The theory of surfactant self-assembly is well-established and can readily be adopted to architecturally complex pre-polymer assemblies. According to the classical protocol which takes water as the solvent, the focus is on amphiphiles which have some hydrophobic moiety (often called the tail) and a hydrophilic one (referred to as head). Examples are CTAB (cetyltrimethylammonium bromide), or SDS (sodium dodecyl sulphate). Such amphiphiles typically pack densely into aggregates called micelles. Ninham and Israelachvili\[16\] have argued that for a classical surfactant the volume of the hydrophobic tail \( v \), the (average) length of the tail \( l \), and the area \( a \) needed to pack the hydrophilic head group are the key elements needed to predict the thermodynamically preferred self-assembled morphology. They introduced a surfactant packing parameter \( P = v / (l a) \). For \( P \leq 1/3 \), the surfactants tend to form spherical micelles. Cylindrical or worm-like micelles are the preferred geometry for \( 1/3 \leq P \leq 1/2 \), while for \( P \geq 1/2 \) the regime is entered where vesicles or bilayer configurations are stable. The use of the surfactant parameter for the current system is not trivial, basically because a precise specification of the head and tail group in the used chain architectures is rather complex. More specifically one molecule may have several, perhaps many tails and/or heads. For example, in one limit the subdivision between heads and tails may take place within side chains of polymers (polysaols). In another limit, a string of hydrophilic monomers is followed by a string of apolar monomers (copolymers) having the same topology as the classical surfactants, but the hydrophilic moieties can also be spread somehow along the molecule. Clearly when the hydrophobic and hydrophilic moieties in the molecules are not classically positioned in a head-tail configuration, the use of the packing parameter is challenging. Within SCF theory, one can easily implement models wherein the polymer architecture is non-trivial and we do not need to identify the head or the tail explicitly. What we need to define is the molecular sequence of the pre-polymer chains as well as the intra/inter molecular interaction parameters (including electrostatic, hydrophobic/hydrophilic interactions, and the interaction with solvent). Details are shown in the modeling parameters section below.

When the amphiphilic polymers are suitable to form stable micellar type assemblies in water, the tails provide the driving force and the head groups provide a stopping mechanism. In other words the tail moieties are apolar, i.e., they do not mix with water, and group together forming a more or less densely packed phase (the core). The polar moieties remain hydrated and are expelled from this core and form a corona layer around the core. With increasing aggregation number, the chain conformations become gradually more elongated in the radial direction. Both the hydrophilic segments in the corona and the hydrophobic segments in the core become strongly stretched in the radial direction (not necessarily to the same extent). It can be shown that a lateral pressure builds up which counterbalances the driving force for further aggregating. As a result some equilibrium aggregation number, \( g \), is negotiated. For non-trivial chain architectures, the balance between driving forces and stopping mechanisms is not easily quantified and in some cases the stretching energy is too high to remove all polar segment from the core and apolar segments from the corona. In such cases, the core cannot be expected to remain dry (as in classical SDS micelles). Polar moieties in the core will facilitate water molecules to be in the core, but obviously there are natural limits. Molecules wherein the segregation between polar and apolar moieties can not sufficiently be realized will not form stable micelles, and such compounds can easily evolve toward macroscopic phase separation wherein the molecules more or less have Gaussian conformations.

2.2. Small Systems Thermodynamics

For a specified geometry, a given number of amphiphilic polymers can assemble into some aggregate. In a cell model approach, the aggregate is placed in the center of the coordinate system. Solving the SCF equations (see Section 2.3) then results in the optimized configuration of these aggregated molecules. Next, it is key to find out whether the aggregate can be identified as a micellar object or whether it is a microdroplet which should grow out into a macroscopic phase when more molecules are added to the cell. It is possible to discriminate between these two options by considering the thermodynamic characteristics. It turns out that for this problem the thermodynamics of small systems\[17\] provides a natural way to arrive at the required information. Within the small systems (cell) approach for a system characterized with an entropy \( S \), a temperature \( T \), pressure \( p \), and volume \( V \), an infinitesimal change of the Helmholtz energy \( F \) can be written as follows:

\[
dF = -SdT - p dV + \sum_i \mu_i dn_i + \Omega_m d V_m, \quad (1)
\]

where \( \mu_i \) is the chemical potential for each molecule type \( i \) and \( n_i \) the number of molecules of that type. In the small system approach, there is an additional term due to the presence of micelles. The micelles are represented by the last term in Equation (1), where \( \Omega_m \) is the grand potential per micelle and \( V_m \) is the number of micelles. The number of micelles is an internal degree of freedom which the
system can use to optimize the free energy:

$$\frac{\partial F}{\partial T_m} = \Omega_m = 0. \quad (2)$$

It follows that in equilibrium the fourth term in Equation (1) vanishes. The use of the fourth term in Equation (1) becomes evident when it is realized that the grand potential $\Omega$ of an aggregate in the centre of the cell can be evaluated using SCF (see Section 2.3). This central micelle is deprived from its translational entropy, and therefore the relation between the overall grand potential per micelle and the one computed by SCF is given by

$$\Omega_m = k_B T \ln \varphi_m + \Omega \quad (3)$$

Using Equation (2), we can compute the volume fraction of micelles for given value of $\Omega$:

$$\varphi_m = \exp \left( - \frac{\Omega}{k_B T} \right) \quad (4)$$

from which it is evident that for relevant cases $\Omega > 0$. We note that Equation (4) can be used to compute the overall surfactant concentration in the cell model for given micelle aggregation number.

Minimization of the Helmholtz energy implies the conditions:

$$\frac{\partial^2 F}{\partial T_m^2} = \frac{\partial \Omega_m}{\partial T_m} > 0.$$

For a given overall amount of polymers, an increase of the number of micelles $\mathcal{N}_m$ will lead to a decrease of the aggregation number $g$. Hence, $\partial \mathcal{N}_m/\partial g < 0$. Moreover, as the volume fraction of micelles does, in a first order approximation, not change when a few bigger micelles are split up into more smaller ones, we conclude that stability implies that

$$\frac{\partial \Omega}{\partial g} < 0. \quad (6)$$

In the SCF calculations, it is possible to evaluate $\Omega(g)$ and the negative slope of this function signals the regime of stable micelles.

Using the Gibbs–Duhem relation $\partial \Omega/\partial \mu = g$, one can easily show that the chemical potential of an amphiphile is also a function of the aggregation number $g$, that is $\mu(g)$. More specifically, for stable micelles we must expect that the chemical potential is an increasing function of the aggregation number.

Finally, it is noted that $\partial g/\partial \mu_{g=g_0} = (g-g_0)^2$ is a measure for the fluctuations in micelle size. Hence, when the chemical potential barely increases with aggregation number we conclude that the micelle size distribution is wide and vice versa. In the same token, we can say that when the grand potential sharply decreases with increasing aggregation number the micelle size distribution is narrow and vice versa.

In general, the following self-assembly picture emerges for spherical micelles. At very low polymer concentrations, no micelles are expected. When the first stable micelles occur most polymers are still freely dispersed and few micelles exist. Upon increasing the polymer concentration, the aggregation number increases, and the grand potential of the micelles decrease accordingly. The micelle concentration grows strongly while the free polymer concentration increases marginally. At some stage, the number of polymers in the solution becomes equal to the number of polymers in the micelles and this may be identified by the critical micelle concentration (CMC), a well-known experimentally accessible quantity. Upon a further increase of the overall polymer concentration, the aggregation number still increases and the grand potential decreases. At some point the grand potential $\Omega = 0$. This corresponds to the condition of an equilibrium micelle when the translational entropy is ignored. In many cases, the micelles at the practical CMC and micelles for which the grand potential vanishes have very similar structure and aggregation numbers (although the latter ones are always a bit larger). In experimental situations, the interest is in the structure of micelles in systems for which the micelle concentration is relatively high and that is why we will present radial volume fraction profiles for micelles at $\Omega = 0$.

As will be shown the central thermodynamic quantity in the SCF theory is the Helmholtz energy of the small system (cell model). When the SCF equations are solved, the bulk volume fractions of all molecules are accurately available and these can be used to evaluate the relevant chemical potentials of all molecular species. Using these, we find the grand potential

$$\Omega = F - \sum_i \mu_i n_i \quad (7)$$

where it is understood that in an incompressible system the $dV$ term not necessary because the volume of the system is exactly specified by total number of molecules in the system (and the volume per molecule). For explicit expressions for the grand potential and the chemical potentials see ref.[18]

2.3. Self-Consistent Field Theory

Here the main elements of the self-consistent field (SCF) theory for (polymeric) self- and co-assembly are outlined using the discretization scheme of Scheutjens and Fleer.[19,20] SF–SCF. It is applied to a molecularly detailed model, wherein the segments in the polymer chain are described on an united-atom level (the united atoms are
referred to as segments below). The theory has been extensively discussed in the literature before and we refer to this for most of the details.\[^{18}\]

At the basis of the SCF theory is the mean-field free energy \(F[\{\psi\}, \{u\}]\). This notation implies that the free energy is a functional of two conjugated profiles, namely the volume fraction (dimensionless concentration) \(\psi(r)\) and the corresponding segment potential \(u(r)\). The free energy is optimized with respect to both distributions. This typically occurs using some numerical method, which invariably requires some sort of discretization scheme. In the Scheutjens–Fleer (SF–SCF) method the space is represented by a set of lattice sites, and the molecules are represented by segments in such a way that one segment fits a given lattice site. For a given problem, one needs to define a particular lattice geometry which allows a three-dimensional system be modeled using concentration gradients in either one direction, two directions, or in three directions. It is obvious that computational efficiency rapidly decreases with increasing number of concentration gradients. For the cases considered here, the classical case of concentric shells along the chain, it is enough to consider one direction. Then a mean-field approximation is implemented for the remaining directions/direction. We focus on a spherical coordinate system (as our main interest is in modeling spherical micelles) with a radial coordinate with lattice layers numbered \(r = 0, 1, 2, \ldots, M\), where \(r = 0\) coincides with the center of mass of a spherical micelle. Each layer has \(L(r) \propto r^2\) sites and the volume fraction if found by the fraction of sites used by a segment type, i.e., \(\varphi_X(r) = n_X(r)/L_r\), with \(n_X\) being the number of sites filled by segment type \(X\).

In slightly more detail, the mean-field free energy can be written as

\[
F[\{\psi\}, \{u\}, \alpha] = \ln Q(\{u\}) - \sum_r L(r) \sum_X u_X(r) \varphi_X(r) + \frac{\alpha}{L} \ln(\{\psi\}) + \sum_r \alpha(r) \left( L(r) \sum_X \varphi_X(r) - 1 \right). \tag{8}
\]

Here and below all energies are reduced by the thermal energy \(k_B T\). \(X\) is an index which runs over all segment types in the system. The first term of Equation (8) represents the partition function \(Q(\{u\}, V, T)\) for the “potential”-ensemble, that is, it can be computed when the potentials are known. Of course, for the implementation of this term we need to specify a chain model and explicit information on the chain architectures. It is instructive to mention that the partition \(Q\) of the system can be decomposed into single chain partition functions \(q_i\) for each molecule of type \(i\)

\[
Q = \Pi_i \left( \frac{q_i}{n_i!} \right)^{n_i}. \tag{9}
\]

where \(n_i\) is the number of molecules (chains) of type \(i\). The single molecule partition function contains the combined statistical weights of all possible chain conformations. We will use the freely-jointed chain model to evaluate this quantity.\[^{21}\] In this chain model, we are going to allow for chain reversals to previously occupied lattice sites, implying that we will not model self-avoiding chains. The rational for choosing this chain model is that there exists a very efficient propagator formalism for the freely-jointed chain model to obtain the single chain partition function, which is easily adopted for molecules with side chains. Basically, \(q_i\) contains the statistical weights of all possible and (in the freely jointed chain model) allowed conformations of molecule \(i\). Let, as an example, molecule \(i\) be composed of a linear chain with \(s = 1\ldots N\) segments, and let \(\delta_i^j = 1\) when segments \(s\) of molecule \(i\) is of segment type \(X_s\) and zero otherwise, one can obtain the potential energy \(u_i^j\) of a given conformation (a specified spatial arrangement of the segments of the chain) \(c\) by summing over the potential energies of the segments along the chain of chain type \(i\):

\[
u_i^j = \sum_s \sum_X \delta_i^j u_X(r_{ij}^s), \tag{10}\]

where \(r_{ij}^s\) is the coordinate of segment \(s\) in conformation \(c\).

Now the partition function is given

\[
q_i = \sum_c \exp(\mp u_i^c). \tag{11}\]

In this form, the computational effort to evaluate the partition function is enormous as the computation effort is proportional to the number of different conformations. Within the freely-jointed chain approximation, the neighboring segments along the chain occupy neighboring lattice sites and positional correlations of segments further apart are basically ignored. For a lattice coordination number (the number of nearest neighbor sites) is \(Z\), there are \(2^{N_i-1}\) number of conformations for given starting position of the chain. As mentioned already, there exists a propagator formalism which generates \(q_i\). The big selling point of SF–SCF is that the propagator formalism allows the evaluation of the partition function with a computational effort proportional to \(N_i\), and this scheme also automatically generates the volume fraction distribution \(\varphi_X(r, s)\). Summing these over all segments, it is straightforward to generate the segment type dependent volume fractions \(\varphi_X(r)\). As a result, we see that the volume fractions can be computed from knowledge of the segment potentials, more formally, \(\varphi[u]\).

The second term in Equation (8) is a Legendre transformation to set the result in the normal \(N,V,T\)-ensemble. Upon a closer inspection, it then turns out that the first two terms of the free energy (Equation 8) essentially give the dimensionless entropy in the canonical ensemble.
The third term in Equation (8) is the contribution that specifies all possible interactions between the different segments and between segments with the solvent, as well as the electrostatic interactions. Electrostatic interactions are accounted by a lattice version of the Poisson equation. This amounts to a term \( \sum \frac{1}{2} q(r) \psi(r) \) in \( F^{\text{int}} \), where \( q(r) \) is the sum of the charges at coordinate \( r \) and \( \psi(r) \) is the electrostatic potential. As usual \( q(r) = L(r) \sum_X \nu_X(r) V_{Xk} e \) with \( V_{Xk} \) the valence of segment type \( X \) in internal state \( k \). The summation over internal states is needed here because in the calculations we will take that the some specified segments will obtain a pH-dependent charge. For more information, we refer to the literatures.\(^{[22–24]}\) The electrostatic potential is found by solving the Poisson equation in the proper spherical geometry. In this equation, the local dielectric permittivity is found by the volume fraction weighted average, that is \( \varepsilon(r) = \varepsilon_0 \sum_X \nu_X(r) \varepsilon_X \) with \( \varepsilon_X \) the dielectric permittivity of vacuum and \( \varepsilon_0 \) the relative dielectric permittivity of a phase composed of segments of type \( X \). The solvency effects are approximated by short-range nearest-neighbor interactions by using the Bragg–Williams mean-field approximation.\(^{[25]}\) Each contact between unlike segments (which is computed based on the local volume fractions) is characterized by a dimensionless Flory–Huggins interaction parameter \( \chi_{XY} \), for contacts between segments of type \( X \) and \( Y \), which is positive for repulsive interactions and negative in case of attraction.\(^{[25]}\) These parameters implement the usual approximation that the like contacts \( XX \) and \( YY \) are taken as the reference, see ref.\(^{[18]}\).

The last term of Equation (8) decouples the volume fractions of the components, where the Lagrange parameter \( \alpha(r) \) is linked to the incompressibility constraint \( \sum_X \nu_X(r) = 1 \), implemented locally for each coordinate \( r \). The indices \( X \) stands for segment types of the molecules (e.g., R, C, O described in Section 2.5).

The free energy still needs to be optimized with respect to its variables. For example, the minimization of the free energy with respect to the volume fraction

\[
\frac{\partial F}{\partial \nu_X(r)} = 0,
\]

or more specifically

\[
u_X = \alpha + \frac{\partial F^{\text{int}}}{\partial \nu_X(r)}.
\]

As can be seen, the segment potential \( u_X(r) \) has a contribution of the Lagrange field \( \alpha(r) \). The derivative of the interaction part of the free energy leads to a couple of contributions. There is term that contains all short-range interactions, \( \sum_Y \chi_{XY} \Psi_Y(r) \), an electrostatic contribution \( V_{XY} \Psi_Y(r) \) and finally a polarization term \( \varepsilon_0 E^2 \), wherein the electric field \( E \) is minus the gradient of the electrostatic potential.\(^{[26]}\) It is easily checked that the potentials \( u \) can be uniquely obtained from the volume fractions, so one should in fact write \( u[\psi] \). We have seen already that the opposite relation also applies and hence the SCF formalism reads formally:

\[
u[\psi] \leftrightarrow \psi[u],
\]

with the constraint

\[
\sum_X \nu_X(r) = 1.
\]

Hence, there is a mutual dependence of the volume fractions and the segment potentials: the potentials both determine and follow from the volume fractions and vice versa. SF–SCF is about \( 10^4 \)–\( 10^5 \) times faster than Monte Carlo simulations. The numerical difference between the input and output potentials determines the numerically accuracy of the SCF solution, which is found iteratively, with an accuracy of seven significant digits.\(^{[20,18]}\)

### 2.4. SCF and Self-Assembly

One can insert the optimized volume fraction profiles and the segment potential profiles in Equation (8) to find numerical values for the free energy. Again, subtracting the chemical potentials \( \mu_i \) of all molecules \( i \) from this free energy gives the grand potential \( \Omega = F - \sum_\mu n_i \). The chemical potentials can be evaluated from knowledge of the composition of the bulk, \( \nu_i \). Here the bulk is the (water rich) phase that exists far away from the micelle. It turns out that the grand potential is the characteristic function that is relevant to analyze the stability of micelles, and closed expressions in terms of the segment volume fraction and segment potentials are available to evaluate the grand potential accurately.\(^{[27]}\)

Even though the SCF model does not require to put constraints on the molecules, that is the polymers and the solvent can freely choose to partition between being in the bulk or in a micellar aggregate, it is required for any SCF calculation to define a particular lattice geometry. Hence in a spherical lattice, one can evaluate the thermodynamic stability of spherical micelles (or spherical vesicles) only. A cylindrical lattice geometry allows us to study linear micelles (end-effects are then typically ignored). Finally, a flat lattice is used to consider the stability of planar bilayers. Using the SCF machinery, it is possible to generate for a given system all these types of association colloids. In general, the chemical potentials of the amphiphiles in these aggregates are a function of the geometry of the associations. The association type for which the molecules have the lowest chemical potential is the preferred one. Below focus is on the use of the spherical geometry.
In the SCF equations, one typically assumes that there is some solvent around the association colloids. Hence, we consider systems which contain a significant, mostly dominating amount of solvent in the system. For example, we consider a central micelle in a spherical coordinate system while a bulk solvent exists at higher values of the radial coordinate. The upper boundary, that is at \( r = M \) we have implemented reflecting boundary conditions. This implies that we imagine that the central micelle is surrounded by neighboring micelles which are a center-to-center distance \( r_m = 2 \times M \) away. By systematically reducing the value of \( M \), one can mimic the response of the central micelle to an increase in micelle concentration. Indeed, by reducing \( M \) the overall polymer concentration in the system will go up and the inter- micellar interaction may cause a transition from spherical micelles toward lamellar phases, or form micelle clusters and gradually phase separate. The local stability of micelles is characterized by the property that the chemical potential of the amphiphiles decreases with increasing intermicellar spacings.

### 2.5. Modeling Parameters

In this paper, we consider PU pre-polymers that are built up by a small set of selected monomer types or building units. Table 1 shows the set of Flory–Huggins parameters used in this study. These are based on previous work and are similar to those used in other studies. The set of Flory–Huggins parameters used in this study is shown in Table 1 and is inspired by earlier surfactant micellization studies. A negative value for a \( \chi \) parameter indicates attractive interactions, whereas positive values for \( \chi \) parameters indicate repulsive interactions. Interactions with the solvent are important and are chosen such that polar groups have a small or negative \( \chi \), whereas the apolar ones have a large positive value as detailed below. Although there is still room to improve the accuracy of the \( \chi \)-parameter based on experiments or atomic modeling, the parameters used here provide a good estimation for the micelle formation of PU pre-polymers. We think that this is the case for the following reason. A pre-polymer with a chemical structure given in Figure 1 has been carefully synthesized, to be reported in a future publication. The predicted self-assembly characteristics as a function of pH and ionic strength follow the experimental data in a semi-quantitative way (not shown here).

### Table 1. List of Flory–Huggins interaction parameters used in the model.

<table>
<thead>
<tr>
<th>( \chi )</th>
<th>S</th>
<th>C</th>
<th>O</th>
<th>R</th>
<th>X</th>
<th>D</th>
<th>A</th>
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<td>0.7</td>
<td>2.3</td>
<td>0</td>
<td>-0.7</td>
<td>1.6</td>
</tr>
<tr>
<td>C</td>
<td>1.6</td>
<td>0</td>
<td>1</td>
<td>0.6</td>
<td>1.6</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>O</td>
<td>0.7</td>
<td>1</td>
<td>0</td>
<td>1.6</td>
<td>0.7</td>
<td>1.6</td>
<td>1</td>
</tr>
<tr>
<td>R</td>
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<td>0.6</td>
<td>1.6</td>
<td>0</td>
<td>2.3</td>
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<td>-1</td>
</tr>
<tr>
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<td>2.3</td>
<td>1.6</td>
</tr>
<tr>
<td>D</td>
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<tr>
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<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1.6</td>
<td>-0</td>
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</table>
The interaction parameters with the solvent S are most relevant for the starting and stopping mechanism of self- and co-assembly. The R unit is taken somewhat more hydrophobic than the C ones. The negative value of $\chi_{SO}$ indicates that the oxygen strongly prefers to be solvated by water. We further implemented a small repulsion between C and R, which is not uncommon as, e.g., CH$_3$ and CH$_2$ also appear to repel each other.$^{[28,29]}$ Further, there is a significant repulsion between O units and apolar units: $\chi_{OR} = 0.1.6$. This repulsion adds to the stability of the micelles. Again these parameters have been used before to model the self-assembly of Pluronics.$^{[26]}$ Moreover, we introduce an extra interaction parameter $\chi_{DA} = -1.6$ to the H-bond donor and acceptor groups, which partially resemble the H-bond interactions of WPUs dispersion. It is noted that this artificial “H-bond” interaction is not directional in contrast to real H-bonds. The chemical sequence of the pre-polymers is the most important factor in determining how self-assembly occurs while being dispersed in aqueous solution. The “H-bond” interaction described here only contributes to the stability of the micelles to a minor extent.

3. Results and Discussion

Let us first consider the self-assembly characteristics of the pre-polymer shown in Figure 1. In a future publication, experimental results will be presented on micellization characteristics of dispersions made from this amphiphilic oligomer. A 1% (w/w) of this oligomer in water at pH 8 and ionic strength of 10 mM resulted in self-assembled micelles with an average diameter close to 15 nm. This seems consistent with our SF–SCF results as will be shown. It is noted that in the molecule the DMPA segments have a pH-dependent charge and for sufficiently high pH this is the most polar moiety in the pre-polymer. The natural complication for self-assembly of this type of pre-polymer is that the charged groups are not ideally positioned at one of the chain ends as is the case for classical surfactants, but that they are distributed along the chain. We first focus on pH 8, at which nearly all the X-groups (carboxylic acid groups) have a negative charge. The focus is on a relatively low ionic strength conditions of 10 mM, so the charges are only weakly screened.

The grand potential $\Omega$, which may be identified as the excess free energy associated with the formation of single micelle, is computed as a function of the aggregation number $g$. The latter quantity is computed for a spherical geometry via

$$g = \frac{\sum L(r)\psi_{pp}(r)}{N_{pp}},$$

where $N_{pp}$ is the number lattice sites occupied by the single pre-polymer sequence.

In Figure 2(a), it is shown that the grand potential of this system in spherical geometry indeed has a negative slope $\partial \Omega / \partial g < 0$ for $g > 20$, which is the characteristic of being able to form stable micelles. A relevant point on this curve is the micelle with $\Omega = 0$. This micelle corresponds to the stable micelle under the assumption that the translational entropy of the micelles can be ignored and is a good approximation for relatively concentrated micellar solutions. For this selected micelle, the aggregation number is $g \approx 80$ pre-polymers. We verified that a spherical micelle is thermodynamically more stable than either cylindrical micelles or bilayers made from this pre-polymer at pH 8 and ionic strength of 10 mM.

Considering the unusual sequence of monomers within this amphiphilic pre-polymer, for which the charged groups are distributed along the chain, inspection of the equilibrium ($\Omega = 0$) radial volume fraction profiles, shown in Figure 2(b), is insightful. As shown in Figure 2(b), the amount of water in the core of the micelle is close to a volume fraction of 0.4. This is rather high compared to for instance SF–SCF computations on block copolymers on pluronics (water core fractions varying between 0 and 0.4, but most are below 0.2).$^{[27]}$ In part the high water content in the core of the micelle in the case of PU pre-polymer micelles may be attributed to the scattered positioning of polar moieties O along the pre-polymer and the non-ideal positioning of the carboxylic acids. As a consequence of the relatively high
The stability of micelles composed of amphiphilic-charged copolymers is greatly influenced by pH and ionic strength of the solution. For the PU pre-polymer charged copolymers is greatly influenced by pH and ionic concentration also affects the formation of the micelles. Within the cell model, the system size is specified by the number of lattice layers $M$ in the system. As reflecting boundaries are implemented, we effectively model a system wherein the inter-micelle distance $r_m$ is twice the value of $M$. We computed the chemical potential $\ln(\varphi^s)$ of the IPDI-polyol-IPDI-(DMPA-IPDI)$_2$ building block sequence as a function of the system size $M$ for various values of pH at a fixed ionic strength of 10 mM. As shown in Figure 4, the chemical potential of the polymer remains stable for $M > 35$ at pH 6, pH 7, and pH 8 indicating that at these distances the micelles do not feel each other. However, when $M < 35$, the chemical potential increases upon decreasing inter-micelle distance. Hence the micelles repel each other, which is the signature of thermodynamically stable micelles. The electrostatic repulsion is the main cause for the repulsion, but the structural rearrangements necessary inside the micelle are also accounted for. We conclude that under these conditions the amphiphilic pre-polymer does form stable micelles.

The electrostatic features of charged micelles are exemplified by the radial profiles for the electrostatic potential, $\Psi(r)$ (in mV), and the corresponding net charge, $q(r) = q(r)/e$ (i.e., the dimensionless charge density) in Figure 5(a). The micelles with a grand potential $\Omega = 0$ (from Figure 3(a)) were selected for this. As a dissociation of carboxylic acid groups introduces negative charges in the micelle, the electrostatic potential in the micelle, $\Psi(r)$, is negative at all coordinates. Moreover, due to the reduced dielectric permittivity in the core region, the total charge density in this region is relatively small, i.e., a charged carboxylic acid group is locally compensated by a positive water content in the core, the chain density in the core never gets extremely high. Further, experimental neutron scattering work on pluronics yielded a water content in the core close to 40%, so our finding is not extreme.

The stability of micelles composed of amphiphilic-charged copolymers is greatly influenced by pH and ionic strength of the solution. For the PU pre-polymer sequence investigated this is confirmed below. It was already mentioned that the pH affects the degree of dissociation of the carboxylic groups. At very low pH, the DMPA groups are uncharged and thus we may expect a reduction of the stopping force with decreasing pH. The ionic strength sets the screening length. For high ionic strength, the charges on DMPA groups are screened and also should deteriorate the stopping force. In Figure 3(a), the grand potential of a spherical micelle is plotted as a function of the micelle aggregation number $g$ (so-called stability curves) at different pH and an ionic strength of 10 mM. Again in such a curve negative slope implies stable association colloids, whereas a positive slope signals the onset of macrophase segregation. Inspection of the graphs proves that stable micelles exist above pH 6. Below pH 6, there is a regime where micelles get unstable. In other words, in the absence of charged DMPA groups micelles cannot form using this pre-polymer sequence.

The concentration of salt will also affect the stability and this point is addressed in Figure 3(b). Here the grand potential of the micelle is plotted as a function of micelle aggregation number at pH 8 for different ionic strength conditions. From this, it follows that stable micelles exist below a critical ionic strength of 30 mM. Increasing the ionic strength to, e.g., 50 mM by adding salt induces screening of charged groups so that the stopping force is too small to arrest the macroscopic phase formation.

On top of pH and ionic strength, the polymer concentration also affects the formation of the micelles. Within the cell model, the system size is specified by the number of
Counterion. When comparing the numbers at pH 6 with those obtained from pH 7, we noticed the overall charge density as well as electrostatic potential curve shift more to the core of micelle upon an increase of the pH. This is in line with the radial volume fraction distribution of negatively-charged carboxylic group \( \text{COO}^\cdot \). As shown in Figure 5(b), the volume fraction of \( \text{COO}^\cdot \) groups also shifts toward the core of the micelle at higher pH, and there is about 30% less charge present in the core of micelle at pH 7 compared to at pH 6.

From above it is clear that the specified pre-polymer, as shown in Figure 1, can form stable micelles at pH 8 and an ionic strength of 10 mM. In practice, however, a rather wide distribution of pre-polymer building block sequences is synthesized and it is of great interest to study the co-assembly of the resulting composite (swollen) micelles. Studies of particle formation based on co-assembly of pre-polymer mixtures help to better understand what determines the internal composition of PU latex particles in practical PU resin dispersions. As explained, we restricted our PU structures such that they are composed of only three building units, namely IPDI, DMPA, and polyol. Using this small set of building blocks, it is possible to construct many other pre-polymer building block sequences without the need to come up with additional FH interaction parameters. As an example, we study here a possible pre-polymer mixture as can be found in practice, numbered 1, 2...6 with the following chain structures: (1) IPDI-DMPA-polyol\(_1\) (this is the amphiphilic pre-polymer used above, and the subscript number indicates the repeating...

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**Figure 5.** Equilibrium (\(\Omega = 0\)) properties related to the charged groups of the PU pre-polymers inside the micelles at pH 6 and pH 7: (a) radial electrostatic potential profile \(\Psi(r)\) (left ordinate) in mV and the corresponding dimensionless charge density \( q(r) \) (right ordinate) of the pre-polymer aggregates in Figure 3(a) at pH 6 and pH 7 (as indicated), and (b) radial volume fraction \(\phi\) of the carboxylic group \(\text{COO}^\cdot\) of the pre-polymer aggregates in Figure 3(a).

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**Figure 6.** (a) Grand potential \(\Omega\) for the pre-polymer mixtures as a function of the representative aggregation number \(g\) (only containing the pre-polymer building block sequence of IPDI-Polyol-IPDI-(DMPA-IPDI)_\(_2\), the volume fraction as well as the molar ratio of the other polymers was fixed as described in the main text and was not counted in this aggregation number). (b) Equilibrium (\(\Omega = 0\)) radial volume fraction \(\psi(r)\) distribution of each pre-polymer as a function of the distance from the (swollen) micelle centre \(r\). The labels refer to (1) IPDI\(_1\)-DMPA\(_2\)-Polyol\(_1\), (2) IPDI-Polyol-IPDI, (3) IPDI-DMPA-IPDI, (4) IPDI-DMPA-IPDI, (5) IPDI\(_1\)-Polyol\(_2\), (6) IPDI\(_2\)-DMPA\(_2\)-Polyol\(_2\), and (7) water.

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The grand potential of the composite (swollen) micelle can again reach zero when the number of molecules of component 1 is increased significantly. Hence, component 1 is able to emulsify the other molecules in such a way that the (swollen) micelle becomes stable. The corresponding stability curve is shown in Figure 6(a). In the accompanying graph, Figure 6(b), the corresponding equilibrium radial volume fraction profiles for the (swollen) micelle are plotted. This radial density profile gives insight into the spatial distribution of the various pre-polymers over the micellar particle. The volume fraction profile of all pre-polymer components and water within the PU (swollen) micelle centre...
micelle is now available. For instance, as described before, component 7 of the pre-polymer mixture used in our model stands for water. It is clear that a significant amount of water is found in the (swollen) micelle core, up to 40%, which is partially attributed to the non-ideal positioning of carboxylic group as explained in the single polymer case and partially due to the H-bond interaction between urea/urethane groups and water. This interaction promotes to get some water entrapped in the core of the (swollen) micelle that mainly consists of the hydrophobic groups of the pre-polymers. The amine groups from urea/urethane are more polar and they also contribute to more favorable interactions with water.

To get a detailed picture of the distribution of the charged DMPA group within the PU (swollen) micelle (this is highly relevant for the performance of WPU dispersion), we also plotted the density profile of all initial building molecules, namely, IPDI, polyol, and DMPA, which were used to make PU pre-polymers via chemical reaction. Instead of presenting the density profile of individual pre-polymer building block sequences, as shown in Figure 6(b), we added up the building blocks of these pre-polymers and plotted the density profile of the building block as a function of \( r \). As shown in Figure 7(a) and (b), the majority of DMPA groups, indicated as a peak in the density profile, is located within the corona of the (swollen) micelle that mainly consists of the hydrophobic groups of the pre-polymers. The amine groups from urea/urethane are more polar and they also contribute to more favorable interactions with water.

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Next, we studied the self- and co-assembly behavior of pre-polymer mixtures with different polyol chain lengths. The molar mass of polyol, polyTHF in this case, was varied between 650 and 1500 Da (the number of repeating units of \( C_4O \), as shown in Figure 1, was varied from 9 to 20). Again, the focus is on the pre-polymer mixtures as described earlier (same chemical structures and relative molar ratios). It was assumed that the chemical composition of the pre-polymer multi-component mixture (molar fraction) does not change upon increasing the polyTHF chain length. All calculations were done at pH 8 and an ionic strength of 10 mM. As shown in Figure 8, all grand potential curves can reach a value of zero, which indicates that pre-polymers using these polyTHF as building molecules can form thermodynamically equilibrium stable (swollen) micelles. It is also indicated that the representative PU (swollen) micelle aggregation number at equilibrium (\( \Omega = 0 \)) increases upon increasing the polyTHF chain length from 76 to 337. This implies that the PU (swollen) micelle size also increases upon increasing the chain length of polyTHF. It follows that PU (swollen) micelles are tunable by rational synthesis: systematic modification of the synthesis of the pre-polymer multi-component mixture with SCF results as input.

![Figure 7.](image1) (a) Volume fraction \( \phi \) profiles of original building monomers (DMPA, IPDI, and polyol) as a function of the radial coordinate \( r \). (b) Volume fraction \( \phi \) of DMPA as a function of \( r \). The chemical composition is identical to the one considered in Figure 6.

![Figure 8.](image2) Grand potential \( \Omega \) for the pre-polymer mixtures with different polyol chain lengths as a function of the aggregation number \( g \). The equilibrium aggregation numbers at \( \Omega = 0 \) are shown along the curves for the various polyol molar masses. The chemical composition is the same as Figure 6, and only differs in molar mass of polyol.
So far, we presented the impact of pH and ionic strength on the micelle formation of single pre-polymer in this paper. It was also shown how each individual pre-polymer and each chemical building block is distributed within the co- and self-assembled PU (swollen) micelle. WPU dispersions are, in reality, more than these PU (swollen) micelles. Especially at high colloid volume fractions, details of the interactions between the (swollen) micelles play an important role. The PU pre-polymer dispersions, described in this work, are only the initial stage of WPU dispersions formation. All kinetics and dynamics effects that might possibly take place during and after polymer dispersion are not taken into account within SF–SCF theory. These factors might also contribute to the final properties of WPU dispersions, their film formation and final coating properties. The influence of micelle concentration was studied using SF–SCF via a variation of the intermicellar distance. This is crucial to explain the transition from a dilute PU (swollen) micelle to WPU dispersions. This aspect will be part of a future publication.

4. Conclusion

Molecularly realistic self-consistent field (SCF) theory has been applied to study the self- and co-assembly of polyurethane (PU) pre-polymers sequences in aqueous solution into a spherical (swollen with educts) micelle. It is shown that detailed information can be obtained on polyurethane particle morphology by using SCF calculations. In a study on self-assembly of a particular PU pre-polymer, it has been demonstrated that the stability of a self-assembled micelle is improved at higher pH, and the micelle becomes less stable when the ionic strength increases. Compared to the self-assembly of the specified PU pre-polymer, co-assembly of complex pre-polymer mixtures illustrates the internal composition distribution of the different building blocks sequences inside a PU latex particle. The distribution of the various compounds within the pre-polymer over the micelle shows the DMPA groups are concentrated at the corona region but are also present in the core of the micelle. Furthermore, we showed that any changes on the building molecule, like the polyol chain length, influences the internal composition of the equilibrium PU pre-polymer (swollen) micelles. It is also found that using a polyol with a higher molar mass will lead to a (swollen) micelle with larger aggregation number.

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