1.1. Polymers and comb copolymers

Any polymer molecule is built up of a large number of repeating units. Each of these can have a very simple chemical structure, as a unit of polyethylene, or be more complicated, as in the case of poly($p$-phenylene-terephthalamide) also known as ‘Kevlar’ or ‘Twaron’.

\[
\begin{align*}
\text{Polyethylene} & : \quad \left[ \begin{array}{c}
\text{H} \\
\text{C} \\
\text{H}
\end{array} \right]_N \\
\text{‘Kevlar’} & : \quad \left[ \begin{array}{c}
\text{O} \\
\text{C} \\
\text{C} \\
\text{N} \\
\text{O} \\
\text{N}
\end{array} \right]_N
\end{align*}
\]

In both examples the macromolecule is linear implying that, if one abstracts from the concrete chemical structure, it can be viewed as a linear thread, or chain, Figure 1.1a. One of the most important consequences of such an approach is that many results in polymer physics are independent of the chemical structure of the molecule but rely heavily on the fact that the degree of polymerization $N$, or, in other words, the molecule’s length, is a very large number, $N \gg 1$, [1–5]. This is a very general assumption, which covers a very diverse class of materials: from synthetic polymers,
1.2. Comb copolymers: Experimental motivation

Comb copolymers display many specific properties arising from their branched architecture [6–24]. First of all, the presence of the side chains strongly influences the conformational behavior of a single molecule. It offers a possibility to control the properties of dilute solutions, including lyotropic behavior in good solvent [13, 14, 20] and adjustment of the molecular dimensions by varying the solvent quality [25, 26] or by quaternization [27]. The precise nature of the side chain attachment (permanent or reversible) is relatively unimportant in this case.

Another aspect worthy of attention is connected to the collective behavior of comb-shaped molecules and concerns the possibility of highly ordered microphase separated states in the melt. There is an opportunity to control the morphology, i.e. shape of the domains, in various ways through modification of the molecular architecture parameters. In contrast to the conformational properties, the melt phase behavior is strongly influenced by the specific, covalent or non-covalent, type of bonding between the main chain and the side chains.

In this section we shall present several examples of peculiar behavior of comb-like macromolecules both in dilute solution and in the melt. The experimentally observed phenomena suggest a variety of the possible applications and may serve as a motivation for our theoretical investigation.
1.2.1. Conformational behavior

We focus first on the change in single molecule behavior induced by the side chains. As pointed out above, the precise nature of the attachment is not of crucial importance in this case, as long as a densely grafted comb copolymer architecture can be achieved. On the other hand, the properties of the side chains, e.g. chemical structure, dimensions, stiffness, mutual interaction, etc, are proven to be a determining factor for the conformational behavior of the complex. This opens an opportunity to control the properties of the final materials by creating (synthesizing) comb-shaped molecules with predefined side chains’ characteristics. Moreover, if it is possible to adjust these characteristics, e.g. interaction, by external stimuli, such as the solvent quality, the pH or the ion concentration, then responsive materials, able to react to changes in their environment, can be constructed.

Here we consider only a few of the possible experimental implementations and applications of the concept presented above.

Lyotropic behavior

In a dilute solution the comb-like molecule adopts a conformation directly related to the solvent quality and side chain length. Under good solvent conditions the affinity of the side chain units to the solvent molecules is higher than to the units of its own kind [1, 2]. This leads to an effective repulsive interaction between the side chains. As a result, if the side chains are long enough, the comb-shaped molecules adopt the conformation of cylindrical brushes, forced by steric overcrowding of the side chains [9–18]. The effective “stiffness” of such a bottlebrush can be much higher than of a bare backbone. In turn, the intermolecular repulsion of the “stiffened” molecules may induce a liquid crystalline ordering even in relatively dilute solutions.

Direct observation of lyotropic behavior of comb-like polymer solutions has been reported by Wintermantel et al. [13]. The comb-shaped macromolecules were synthesized from so-called macromonomers, i.e. end-functionalized oligomers, by means of radical homopolymerization reaction resulting in a main chain degree of polymerization up to 1000. From the X-ray patterns measured one can clearly observe a peak at the scattering vector values \( q \approx 0.04 - 0.06\,\text{Å} \), which cannot be explained by single-particle scattering but reflects the interparticle structure factor \( S(q) \) originating from the intermolecular order of the molecules.

Besides the observation of liquid crystalline ordering, an indirect measurement of the molecule’s stiffness has been performed by a number of researchers [13, 14,
1.2. Comb copolymers: Experimental motivation

Figure 1.2: Cylindrical core-shell brush molecule in (a) good for both blocks and (b) good for PAA but poor for PS solvent.

20, 28]: fitting the measured radius of gyration versus molar mass curves by a worm-like chain model [29] one can extract the Kuhn segment length $l_K$. Basically, two important conclusions can be drawn from these measurements. First of all, as a result of the side chains attachment the main chain indeed adopts an extremely stiff conformation, i.e. the Kuhn statistical segment length is of the order of the overall backbone length. Secondly, the stiffness of the entire molecule strongly depends on the side chain length. Taking the above cited [14] polymacromonomers as a characteristic example, one observes an increase in the effective Kuhn length from $l_K = 890\text{Å}$ to $l_K = 2076\text{Å}$ if the side chains molar mass increases from 2780 g/mol up to 4940 g/mol.

Responsive molecules

As explained above, the side chains repel each other under good solvent conditions. The “strength” of the repulsion is determined by the solvent quality. Thus, adjusting the latter, we can manipulate the properties of a single molecule.

The main chain can be considered as a statistical coil or, in other words, an entropic spring, which resists stretching. On the other hand, the repulsion between the side chains makes such stretching favorable. This ultimately leads to the length variation of cylindrical brushes upon a change in the solvent quality for the side chains. Indeed, as has been reported by Fischer and Schmidt [25], variation in the solvent quality leads to a change in the length of the rod-like molecule. Polymacromonomers (PS with a methacryloyl end group) were investigated by static and dynamic light scattering in tetrahydrofuran and cyclohexane. The corresponding contour lengths per monomer were extracted from the fitting procedure and showed an increase
from 0.11 nm to 0.145 nm when going from cyclohexane to tetrahydrofuran. Note, however, that this is still far away from the all-trans 0.253 nm value.

Such polymers seem to be suitable as responsive materials for sensors or actuators if a directional orientation of the cylinders is achieved. This can certainly be done: the bottlebrushes are shown to form lyotropic phases (see the previous example). Fischer and Schmidt [25] also suggest an alternative way to control the length of the combs – cylindrical polyelectrolyte brushes’ length can be controlled via the ionic strength.

Another example of solvent-controlled molecular dimensions is presented by Cheng et al. [26]. The polymer brushes synthesized have diblock side chains consisting of two chemically different blocks: polystyrene (PS) and poly(acrylic acid) (PAA). Upon the solvent quality change from good for both PS and PAA to good for the PAA (outer) and poor for the PS (inner) block, the PS core contracts drastically, Figure 1.2, as follows from the $^1$H NMR spectrum. This allows to construct nanocylinders with well defined core-shell structure, the core (or shell if the diblocks are attached by the PAA end) size of which can be externally controlled.

**Molecular nanowires**

Due to the well-defined core-shell structure, comb copolymers with diblock side chains can be utilized as nanocontainers or nanoreactors. The formation of nanowires [30] on the basis of a brush with polystyrene backbone plus poly(vinyl-2-pyridine) (PVP) side chains is one of the promising examples in this direction.

The PVP core of the cylindrical brush, Figure 1.3, was loaded with H\text{AuCl}_4 in toluene or methylene chloride solution (analogous results were attained with cylinders loaded with CuCl$_2$, H$_2$PtCl$_6$, and CoCl$_2$). This process was followed by reduction of the noble metal salt by an electron beam, by ultraviolet light, or by chemical reducing agents. A continuous nanowire was formed under certain conditions most probably within the core of the cylindrical brushes. It should be noted that the observed length of the wires was much higher (several micrometers!) than the length of an individual molecule – this effect resulted from a peculiar end-to-end aggregation of the brushes. The aggregates formed indeed resemble conventional wires very much: the conducting core is surrounded by a PS shell, which can serve as an electrically insulating layer. Moreover, the properties of the conducting core can be influenced, for instance, during the reduction process, leading to complexes with different conductivities. However, the direct conductivity measurement still remains a challenge.
1.2. Comb copolymers: Experimental motivation

Figure 1.3: Schematic illustration of a nanowire formation. Core–shell cylindrical brushes with a PVP core and PS shell are loaded with HAuCl$_4$. Subsequent reduction yields a one-dimensional gold phase within the macromolecular brush.

“Shaped” molecules: horseshoe- and meander-like structures

Not only the linear dimensions but also the shape of the comb-like polymer can be controlled via adjustment of the side chain parameters, e.g. interaction. Peculiar horseshoe- and meander-like conformations were observed by Stephan et al. [27] in the system consisting of two types of side chains, polyvinylpyridine (PVP) and polymethylmethacrylate (PMMA), grafted to a common backbone. Depending on the solvent, the copolymer brushes were shown to adopt different shapes – from worm-like to horseshoe- and meander-like structures – when spin-cast on mica, Figure 1.4. Due to the unfavorable interaction between the PVP and PMMA side chains (it was additionally boosted by quaternization) the side chains have been “phase separated” to different sides of the backbone. The inhomogeneous distribution of the different side chain types along the main chain and the presence of the selective solvent made the curved structures formation favorable. In principle, the curvature could be also induced by different length, volume, and/or interaction of the PVP and PMMA chains.

The above example shows that the shape persistent synthetic macromolecules can be chemically manipulated to change their conformations from worm-like to
Figure 1.4: Sketch of the phase separated side chains in a horseshoe brush (left) and in a meandering brush (right). The selective solvent is good for the thick and poor for the thin side chains.

regularly curved structures. Finally, it should be mentioned that peculiar spiral conformations of pure PMMA brushes deposited from a dilute solution onto mica have been observed as well [31]. However, the adsorption process itself was assumed to be responsible for the uneven side chain distribution making the “shaping” process much less controllable.

The number of the experimental results published (see, e.g. [15, 16, 18, 19, 23, 24, 32–34]) goes far beyond and is far more diverse than the examples presented here. Two general conclusions about conformational properties of combs can be drawn: (i) Stiffness of the bottlebrushes is a result of the repulsive interaction between the side chains; the length of the side chains, their grafting density, and the quality of the solvent play an important role. (ii) Dimensions and shape of the molecule are strongly influenced by changes in the strength of the side chain repulsion, i.e. can be controlled by adjusting the solvent quality, the ion concentration, using adsorption on surfaces, employing chemically different side chains, etc.

1.2.2. Phase behavior and microstructure formation

So far, we considered solutions of individual comb-like polymers emphasizing the side chain influence on the conformational behavior of the whole molecule. However, the melt state is equally interesting. As pointed out above, in many cases comb copolymers consist of a backbone and side chains, that are chemically different, generally disliking each other. This was not important under the conditions considered above: the contact area between these two was negligible due to a good
1.2. Comb copolymers: Experimental motivation

Figure 1.5: Schematic representation of the three classical morphologies, from the left to the right: lamellar, cylindrical (hexagonal lattice), and spherical (body-centered cubic lattice). The diblock molecule consists of a gray and a white blocks.

solvent. Apparently, this situations is reversed in the melt where, in principle, each backbone can be completely surrounded by its own and the neighbors’ side chains, giving rise to a highly unfavorable interaction. The strength of this interaction, or, in other words, the mixing free energy, is commonly described in terms of a Flory-Huggins interaction parameter [1], which describes the free energy cost per monomer (in $k_B T$ units) of contacts between two chemically different units. Correspondingly, the “penalty” for the entire molecule is proportional to $\chi N$, where $N$ is the overall degree of polymerization.

To explain the possible consequences of the repulsion, we will use a somewhat simpler example of a copolymer system, namely a diblock copolymer, which consists of two types of homopolymers linked together. Driven by the mutual repulsion between chemically different monomers, but unable to macrophase separate due to the covalent bond between blocks, they form mesoscopic ($\sim 10\text{nm}$) domains filled with one or the other component, i.e. microphase separate [35–37]. Depending on the domain shape one distinguishes different morphologies, e.g. Figure 1.5. Domains themselves are generally organized into a periodic structure, therefore the process is also called self-organization.

The morphology of the microphase separated diblock melt is determined by the value of the $\chi N$ parameter (note that $\chi$ is temperature dependent) and the molecule composition $f$ and depends only weakly on the other parameters, like monomer size or shape, implying that their change influences the phase boundaries only a little. On the other hand, architectural changes can be much more effective at shifting phase
boundaries [38] in the direction needed for a certain application without a change in the chemical composition. Apparently, this is the point where the comb-shaped polymers become particularly interesting.

The precise nature of the comb-like molecules system is very important. In the case of hairy-rods (see Figure 1.1e) [39–41] the stiff backbone, for instance, limits the set of accessible morphologies to hexagonal and lamellar. Furthermore, the chemical nature of the bond between side and main chains also strongly influences the phase behavior of the system. Here we will briefly discuss the peculiarities of the (micro)phase equilibria observed in the comb copolymer hairy-rod system, first with covalently and then with reversibly bonded side chains.

**Covalent hairy-rods**

Self-organization in hairy-rod systems received a lot of attention, in particular, in the context of electrical conductivity (see [42] and references therein), since there the backbones consist of conjugated rigid polymers.

Unsubstituted rigid rod polymers have typically a high melting temperature, e.g. ca. 600°C for the polyester poly(1,4-phenylene 2,5-di-\(n\)-alkoxyterephthalate) with side chain length \(n = 0\). However, even a short alkyl tail of length \(2 < n \leq 6\) reduces substantially the melting temperature (to 250–300°C) and a transition from a crystalline to a nematic phase is reported for the above mentioned polyester [39, 43]. For longer side chains, the melting point is reduced further, for example for \(n = 12\) it is 150°C. However, as the nonpolar side chain becomes longer, i.e. \(n \geq 8\), the repulsion with the backbone becomes correspondingly larger. Therefore, one enters into the regime of self-organization, where the alkyl tails and the backbones microphase separate and a layered structure is formed [39, 41, 43–46].

A literature survey shows that in most cases the self-organization is in the form of lamellar structures. For example, the self-organized structures in bulk of alkyl substituted polythiophenes have been systematically studied by Winokur et al. [47] and Chen and Ni [48], demonstrating the formation of self-organized lamellar phases for \(n \geq 4\). A further example concerns poly\((p\)-phenylene\)) (PPP), which is an insoluble and infusible conjugated polymer. Based on this polymer, Wegner et al. prepared several different types of hairy rods [49–51]. Poly(2,5-di-\(n\)-dodecyl-1,4-phenylene) contains two flexible alkyl tails at each aromatic ring [50]. In the solid state a self-organized lamellar phase is obtained with a long period of ca. 35Å at room temperature. Upon heating the long period slightly decreases until at ca. 190°C an ODT to a disordered state occurs. A modification is reported where the alkyl
1.2. Comb copolymers: Experimental motivation

Side chains have been replaced by alkoxy chains [51]. For octyloxy and dodecyloxy side chains \( n = 8, 12 \), lamellar self-organized structures are obtained. However, for shorter butoxy or pentoxy tails \( n = 4, 5 \) the distribution of side chains around the polymer backbone was described as approximately cylindrical. These side chains are probably too short to induce microphase separation.

Hairy-rod architectures involving polyaniline with covalently bonded side chains is yet another example. The emeraldine base (EB) form of polyaniline consists of alternating amine and imine repeat units. Side chains have been introduced by covalent connection of short alkyl (methyl or ethyl) chains to the aromatic rings [52] or by a series of different long alkyl chains ranging from butyl to octadecyl to the aminic nitrogens [53]. Levon et al. [54] prepared N-alkylated polyaniline starting from leucoemeraldine, the completely reduced form of polyaniline. Products with octyl or longer side chains showed strongly improved solubility in common organic solvents such as chloroform, toluene, etc. In the bulk state self-organized layered structures are formed with a long period linearly increasing from ca. 20Å to 32Å as a function of the side chain length [54].

Many more examples [55] can be given, all demonstrating that bulk systems consisting of hairy-rod polymers self-organize due to microphase separation between the backbone and the side chains if the side chains are long enough. In almost all cases a layered structure is found. It should, however, be realized that in all cases the length of the side chains involved is relatively small.

**Supramolecular hairy-rods**

As discussed above, self-organization is an example how nanoscale structures can be formed if different repulsive chemical groups are chemically connected to the same molecules. By contrast, in supramolecular chemistry linking occurs via functional groups that are mutually connected by molecularly matching physical interactions, such as hydrogen bonding, \( \pi \)-stacking, charge transfer, steric match, interpenetrating ring-like structures etc [56, 57]. Using molecular recognition highly specific complexes can be build, which, in turn, are able to form a hierarchy of structures. Self-organization and supramolecular concepts can naturally be combined to allow structuring [58–61].

The possibility of obtaining comb copolymer structures via the supramolecular route, using physical matching interactions, such as ionic, coordination or hydrogen bonding has attracted a lot of attention lately. Most systems studied involve flexible polymers. However, since the synthesis is so simple, i.e. common precipitation in
water for polyelectrolyte-surfactant complexes \cite{59, 62, 63} or solvent casting from a common solvent in the case of hydrogen bonding \cite{64}, the natural question arises whether hairy-rod polymers can be prepared via a similar supramolecular route, i.e. can hairy-rod molecules be synthesized by simply connecting side chains by "recognizing" driven physical bonds? In the case of rigid rod polymers, the drastically reduced solubility is a most complicating factor. Still a few examples, where this concept works, have been constructed recently.

Rod-like (conjugated) poly(2,5-pyridinediyl) (PPY), camphorsulfonic acid (CSA) and selected alkylphenolic type amphiphiles were combined to form supramolecules that form self-organized structures due to protonation, synergistic hydrogen bonds and polar nonpolar effects combined. PPY was first complexed with CSA to form PPY(CSA)$_x$ ($x$ denotes number of CSA molecules per pyridinediyl). Amphiphilic molecules, such as 5-pentyl-1,3-dihydroxybenzene (PRES), 4-hexyl-1,3-dihydroxybenzene (HRES), octyl phenol (OP) or octyl gallate, i.e. 1-octyl-3,4,5-trihydroxybenzoate (OG), were hydrogen bonded to PPY(CSA)$_x$, resulting in hairy-rod complexes denoted as PPY(CSA)$_x$(amphiphile)$_y$. The main observations were that for small $x$ and $y$, e.g. $x = 0.25$, $y = 0.25$ or 0.5, between 25 – 200°C a glassy birefringent material was obtained. For increased values, $x = y = 0.5$, a glassy material was observed at 25°C but at moderate temperatures, a birefringent fluid was formed. X-ray diffraction curves showed typically several very sharp reflections following the sequence $q^*, 2q^*, 3q^*, \ldots$, indicating a lamellar structure. Further increase of $x$ and $y$ resulted in a liquid crystalline state even at 25°C and a transition to an isotropic (non-birefringent) disordered fluid at a higher temperature. If $y/x > 2$, a biphasic system was typically seen. Qualitatively the same behavior is observed for all the above amphiphiles.

Slightly different system, consisting of rodlike PPY complexed with methanesulfonic acid (MSA) and further with OG, was under the scope as well \cite{65}. The PPY(MSA)$_{1.0}$(OG)$_y$ complexes were made in dilute solutions of formic acid followed by evaporation and drying in vacuum and then studied using small-angle X-ray scattering (SAXS). A strong tendency for self-organization has been observed and a microphase separation occurred already when a little OG had been added. For small $y$ the structure is relatively poor, but when $y$ is increased the cylindrical cubic phase is observed for $y = 0.5$ and $y = 0.75$. Increasing $y$ further, at $y = 1.0$, an oblique lattice most likely comprising of elongated or elliptical self-organized domains is seen. A single cylindrical micelle contains now ca. 9 parallel polymer chains in the cross section. The lamellar phase appears for $y > 1.5$ (110°C $< T < 180$°C), whilst
for $y > 2.0$ free OG starts to macrophase separate.

These examples demonstrate that it is possible to form processable supramolecular hairy-rod polymer systems. Furthermore, the self-organization due to microphase separation between the backbone and the side chains (of moderate length) gives rise to a layered structure as in the case of covalent hairy-rod polymers. In addition, however, two other structures can be observed (cubic and oblique), and there is a strong tendency for macrophase separation.

1.3. Conformational behavior: Theoretical results

The conformational properties of the comb-like macromolecules have been studied theoretically by several authors [31, 66–87], using both analytical approaches [66–73, 81, 82, 88] and computer simulations [31, 73–80, 83–87]. Apparently, the side chain induced stiffness of the comb copolymers is one of the most studied problems [66–68, 73, 74, 76–80]. Recently, the peculiar conformations of comb-shaped polymer molecules received considerable attention as well [31, 81, 82, 84].

1.3.1. Lyotropic behavior of the cylindrical polymer brushes

The idea that the presence of branches should cause an increase in the excluded volume effect and therefore the expansion of the branched polymer above that of its linear counterpart, is quite old. Already in early sixties this conclusion was drawn by Kron and Ptitsyn [89] and Berry and Orofino [90]. They assumed the excluded volume to be small and took it into account in the framework of a perturbation theory. Apparently, such an assumption fails in reality as shown, for instance, by recent experiments [13, 14, 20, 28]. Accordingly, the deviations from ideal behavior, i.e. induced stiffness of the molecule and expansion of the side chains, are the main concerns of the more recent theories.

The stiffness of a macromolecule is traditionally described by its persistence length $\lambda$ and the side chain attachment results in its increase. Another parameter of the bottlebrush, its diameter $D$, Figure 1.6, describes the dimensions of the side chains. The ratio $\lambda/D$ plays an important role in the polymer system: as discussed by Khokhlov and Semenov [91], lyotropic behavior of semiflexible chains becomes

---

1 The persistence length is a correlation length along the chain (the backbone in the case of combs), which is defined [2] as: $\langle n(0)n(s) \rangle = \exp(-s/\lambda)$. Here $n(s)$ is a tangent to the chain unit vector, $s$ is a curvilinear coordinate along the chain [2].
possible if this ratio is sufficiently large, say of the order of ten or more. Hence, the prediction of the $\lambda/D$ parameter is one of theoretical challenges.

**Scaling approach**

One of the first predictions of the local conformational structure and dimensions of long comb-like polymers in a good solvent was made by Birshtein et al. [66] on the basis of scaling arguments. They considered a simple comb molecule consisting of side chains of degree of polymerization $N$ grafted to a backbone, which has $N_b$ monomeric units. The grafting density is described by the number of main chain segments $m$ (see the inset (a) in Figure 1.6) between two successive side chains, $N_b \gg N \gg m \gg 1$. First, a cylindrical brush with a fixed grafting distance $b$ was considered, yielding

$$ D \sim N^{3/4} b^{-1/4} $$

(1.1)

for the diameter of the molecule. Afterwards, the elasticity of the main chain between two successive grafting point was taken into account and the distance $b$ obtained in the form

$$ b \sim m^{2/5} \left( N/m \right)^{3/25} $$

(1.2)

Combining (1.1) and (1.2) together one concludes that the side chains have an end to end distance $D \sim N^{18/25}$ with an exponent, which is only slightly smaller than that of a 2D self-avoiding walk (0.72 vs 0.75). As the authors also argued, but not proved, that the increase in the main chain rigidity scales in the same way as the dimensions
of the side chains, it followed that

\[ \frac{\lambda}{D} \sim 1. \]  

(1.3)

This prediction implies that the side chain attachment has negligible influence on the lyotropicity – a result contradicting the more recent experimental data [13].

A somewhat different approach was employed by Fredrickson [67] who predicts \( D \sim N^{3/4}b^{-1/4} \) in the high grafting regime but considers the distance \( b \) to be constant (inset (b) in Figure 1.6). The persistence length \( \lambda \) is obtained as an elastic constant describing the free energy per unit length change \( \Delta F \) upon bending of the molecule

\[ \frac{\Delta F}{k_B T} \sim \frac{\lambda}{R^2}, \]  

(1.4)

where \( R \) is the radius of curvature. Fredrickson modified the Daoud–Cotton method [92] to analyze the toroidal geometry and, in particular, to take into account a slight redistribution of the side chains from the inner half to the outer half of the bent brush. The resulting prediction for the persistence length

\[ \lambda \sim N^{15/8}b^{-17/8} \]  

(1.5)

leads to a positive exponent in the \( \lambda/D \) scaling law

\[ \frac{\lambda}{D} \sim N^{9/8}. \]  

(1.6)

Such an exponent value close to 1 means that the stiffening effect should be pronounced and the rigidity, required to enter the liquid crystalline regime, should be easily achieved by making the side chains long enough.

Finally, a Birshtein-like approach was employed by Zhulina and Vilgis [69], but with bending elasticity effects taken into account more accurately. The predicted ratio \( \lambda/D \sim (N/m)^{9/10} \) is also in favor of lyotropicity in solution.

**Self-consistent field approach**

Recently Subbotin et al. [68] calculated the characteristics of a comb-like molecule in the framework of the analytical self-consistent field approach (SCF). The free energy of a side chain includes an entropic stretching term and the energy of excluded volume interaction. These two effects are connected because the side chains...
surrounding the test chain are responsible for its stretching. The SCF approach takes
the stretching into account by introducing a field “induced” by the neighbors and
coupled to the mean monomer density (self-consistency condition). To obtain the
persistence length, first a straight cylindrical brush was considered and the bending
effects are then addressed as a perturbation.

The starting point in the SCF theory is the side chain free energy written in the
form

\[
\frac{F}{k_BT} = \int dV\left[ -g(\mathbf{r}) \ln Z_N(\mathbf{r} | \mu) - \mu(\mathbf{r}) c(\mathbf{r}) + g(\mathbf{r}) \ln g(\mathbf{r}) + \frac{v}{2} c^2(\mathbf{r}) \right].
\] (1.7)

The side chain under consideration is supposed to be grafted at the origin \( r = 0 \)
and have its free end at point \( \mathbf{r} \) with probability distribution \( g(\mathbf{r}) \). The parameter \( v \)
describes the excluded volume interaction between side chains, taken into account in
the second virial approximation (see the last term in (1.7), where \( c(\mathbf{r}) \) is the monomer
density). \( Z_N(\mathbf{r} | \mu) \) is the partition function of a chain with the free end fixed at \( \mathbf{r} \) in
the external (conjugated to the density) field \( \mu(\mathbf{r}) \). The elastic stretching is described
by the first two addenda in (1.7). The first of them is equal to the free energy
of a chain stretched to the end-to-end distance \( |\mathbf{r}| \) by the external field \( \mu(\mathbf{r}) \). The
second one subtracts the energy due to interaction with this field. Consequently, their
combination represents purely entropic stretching of the side chain. Finally, the third
term is responsible for the translational entropy of the free end.

The self-consistency condition \( \delta F/\delta c = 0 \) immediately yields: \( c = \mu/v \). Func-
tions, such as \( g(\mathbf{r}) \) and \( \mu(\mathbf{r}) \), have to be found from the extremum conditions for the
functional (1.7), whereas the partition function \( Z_N(\mathbf{r} | \mu) \) can be obtained from the
well-known relation [2]

\[
\frac{\partial Z_m(\mathbf{r})}{\partial m} = \frac{a^2}{6} \Delta Z_m(\mathbf{r}) - \mu(\mathbf{r}) Z_m(\mathbf{r}) , \] (1.8)

where \( a \) is a statistical segment length. The authors employ the analogy between (1.8)
and the Schrödinger equation to search its solution in the form of the semiclassical
approximation [93]

\[
Z_m(\mathbf{r}) \sim \exp (-mE - S(\mathbf{r})) . \] (1.9)

In fact, this means that the chain conformations are considered as trajectories of
classical particles moving in an external potential \( \mu \). The constant \( E \) and function \( S(\mathbf{r}) \)
introduced in (1.9) are nothing but the energy of the particle and its action. In order to simplify the calculation, one makes use of the Alexander–de Gennes approximation [94] \( g(r) \sim \delta(r - D/2) \), i.e. assumes all side chain ends to be located at the same distance \( D/2 \) from the backbone. After an appropriate calculation the brush diameter is obtained as

\[
D = 0.92a \left( \frac{v}{a^2 b} \right)^{1/4} N^{3/4} \sim N^{3/4} b^{-1/4}
\]

in complete agreement with the scaling prediction (1.1).

Using the perturbation scheme with a small parameter \( D/R \), the same approach can be employed to analyze a bent brush with radius of curvature \( R \). The main result of such a calculation is the persistence length \( \lambda \)

\[
\lambda = 0.047 \frac{vN^2}{b^2} \sim N^2 b^{-2}.
\]

Note that this result is quite close to the Fredrickson’s prediction (1.5). Accordingly,\[ \frac{\lambda}{D} \sim N^{5/4}, \]

which differs only slightly from the 9/8 exponent law (1.6). This relatively good agreement can serve as an additional argument supporting both theories.

**Computer simulation studies**

Comb-like macromolecules have been extensively studied by means of computer simulations during the last decade. The role of the simulations is twofold. First of all, they can be considered as a “clean” experiment in order to verify the proposed theories since in many cases a real experiment would involve much more complicated structures than the analytically solvable models describe. Furthermore, computer simulations are very useful to predict the behavior of comb molecules taking into account much more fine effects than is affordable in the theory (e.g. semi-flexibility of side chains).

Due to relatively large structures to be studied, the researchers adopted mainly Monte-Carlo techniques [95] to sample the phase space of the molecule. Still, simulation time remains one of the main computational problems restricting the system size. That is why long side chains were almost unaccessible in early simulation work [96, 97].
In the mid-nineties Rouault and Borisov [73] performed a lattice MC simulation mainly to verify their own theory presented in the same paper. The largest system studied included a backbone of 800 monomers with 80 side chains of 35 monomers each. Despite the quite impressive size of the system (in total 3600 monomers) it cannot be called densely grafted: a grafting distance of 10 units is not small if compared to the Flory radius \( R_F \approx 35^{3/5} \approx 8.4 \) units. This explains the dependence \( D \sim N^{3/5} \) obtained for the side chain size, which is specific for unperturbed three dimensional SAW chains. The authors also pointed out that the traditional bond fluctuation model (BFM) led to extremely long relaxation times, around 1 CPU month. Due to this reason a much more effective pivot [98] algorithm was employed in the subsequent publication [74]. This allowed to increase the grafting density and \( D \sim N^{0.7} \) was obtained, which is much closer to the predicted [66, 67] values. However, the elastic properties were not considered in either of the two papers because of strong scattering in the data needed for the persistence length calculation.

A quite thorough investigation of the influence of the side chain rigidity and thickness on the comb molecule elastic properties was presented by Saariaho and co-workers [78–80]. The induced rigidity was proven to be more pronounced in the case of stiff side chains resulting in a \( \lambda \sim N^2 \) law. For rigid side chains the \( \lambda/D \) ratio then obviously satisfies \( \lambda/D \sim N \) in perfect agreement with a recent theory [70]. It is important to note that the theoretically hardly accessible intermediate regime of semi-flexible side chains was also addressed [79]: the persistence length increased as a function of the side chains stiffness. Finally, the authors showed [80] that the ratio \( \lambda/D \) depends strongly on the side bead size, indicating the importance of the side chain topology and the possibility to attain the liquid crystallinity regime by proper side chain chemistry.

More simulation works are available [83, 99] generally employing a lattice BFM algorithm to sample the configuration space. However, direct estimation of the persistence length remains outside their scope and they mainly focus on the cross section diameter and radius of gyration of the comb-like molecule.

A few conclusions can be made on the basis of the simulation studies available. First of all, in the majority of papers the size of the system studied is quite far from the asymptotic regime described by theories. Thus, simulation of large enough structures to make a direct comparison with the theory still remains a challenge. Another important point, which can be learned from the simulation data, is that the lyotropicity can be induced not only by increasing the side chain length but also by changing intrinsic parameters of the side chain (flexibility, monomer size, etc) directly related
1.3. Conformational behavior: Theoretical results

1.3.2. Related problems

Peculiarities of the bottlebrushes’ conformational behavior are not limited to elasticity and lyotropicity. Here we mention briefly some other issues concerning a single molecule conformation where the presence of side chains plays a determining role.

Generally, researches assumed that the comb molecule already reached the bottlebrush regime implying that the Flory radius strongly exceeds the grafting distance, \( R_F = a^{2/5} v^{1/5} N^{3/5} \gg b \), where \( a \) is the statistical segment length and \( v \) is the excluded volume parameter. However, the question about the crossover between star and comb regimes is also interesting by itself. Very recently Denesyuk [100] presented a renormalized perturbation theory analysis supported by scaling arguments to identify two crossovers: between star and bottlebrush, and between bottlebrush and coil. The first one appears when the backbone size becomes comparable to that of the side chains. Beyond a certain point the swelling of side chains drastically slows down, and upon further growth of the backbone length the molecule starts to resemble a stiff cylinder, i.e., a bottlebrush. Further, when the backbone size exceeds the persistence length \( \lambda \), it starts to bend. This marks the second crossover, after which the brush adopts a coiled conformation when the length of the backbone is very large.

Another interesting aspect of the conformational behavior is that the cylindrically shaped bottlebrush conformation is not always the most stable shape of the molecule. Experiments with strongly adsorbed molecular brushes by Möller, Sheiko and co-workers [15, 16, 18, 31–33] stimulated a series of theoretical works [81–83], aiming to explain the experimental results and, in particular, the peculiar curved conformations observed [31]. As shown in [82], instability of the straight backbone can be caused solely by the entropic elasticity of the side chains. If they are allowed to flip over and change their position with respect to the backbone, a smaller extension can be attained upon their uneven distribution. In turn, the induced asymmetry leads to a spontaneous curvature, as also explained in [81] and [83]. The instability is strongly influenced by the length of the side chains \( N \) and the curved conformations should occur for \( N > (\lambda_s \lambda_b / a^2)^{1/3} \), where \( \lambda_s, \lambda_b, \) and \( a \) are the side chain and backbone persistence lengths and statistical segment size respectively.

The effects of attraction between the side chains (e.g. hydrophobic side chains and hydrophilic backbone in water, [101–104]) attracted an increasing interest as well. Apparently, it results in the formation of much more compact structures than bottlebrushes. One of the first computer simulation studies was presented by Rouault
and showed that the coil-globule collapse transition of the comb molecule results in a drastic decrease of its size in a narrow interval of attraction energies between monomers. An analogous system was studied by Vasilevskaya et al. [84] who found that the resulting globule has a complex structure: in the case of a long backbone, the side chains form several spherical micelles while the main chain is wrapped on the surface of these micelles and between them. Effects of the attraction in 2D have been studied by Flikkema and ten Brinke [86] for rigid side chains. A considerable contraction of the comb was observed if the attraction energy per monomer was increased. If side chain flipping was allowed, the attraction between the side chains led to aggregation of successive side chains at one side of the backbone resulting in a characteristic local spiraling of the backbone.

More examples of theoretical studies [71, 85, 87] can be given all supporting the idea that the comb-like copolymer molecule’s shape can be manipulated by architectural, chemical, or external factors allowing to attain the desired conformation.

1.4. Phase behavior and microstructure formation: Theoretical results

Self-organization in block copolymer melts attracted enormous attention not only because of the theoretically challenging problems but also due to its commercial and biological importance. Despite the qualitatively rather simple physics behind the phenomenon (see section 1.2.2), an exact explanation of the observed effects requires deep insights and quite cumbersome calculations.

Diblock copolymers are at the moment the most thoroughly studied system: the theoretical phase diagram calculated in the mean-field approximation reproduces the experimentally observed one reasonably well. Coarse-grained mean-field theories, allowing to reduce the problem from a many-body to a one-body problem, proved to be very productive in this area. They are generally categorized in one of three groups: weak segregation limit (WSL), strong segregation limit (SSL), and full self-consistent field theories (SCFT). To some extent, the first two can be considered as analytical approximations to SCFT corresponding to weakly- and strongly-segregated melts. The WSL was introduced by Leibler [105] and is valid in the vicinity of the critical point. Despite this serious limitation, WSL theory provides a nice explanation of the structure of the mean-field phase diagram. The opposite SSL deals with a completely separated melt, where contacts between chemically different monomers take place.
only in a narrow region [106]. This corresponds to large values of \( \chi N \), as commonly believed \( \chi N > 1000 \). The so-called full self-consistent field theory, introduced in the Fourier-space formulation by Matsen and Schick [107], is more numerically driven and, in principle, can achieve an arbitrary accuracy, thus, connecting weak and strong segregation regions.

A number of valuable reviews [35–37, 108] are available discussing, in particular, advantages and disadvantages of the methods mentioned. Here we will focus on the case of comb-like molecules.

### 1.4.1. Comb copolymers with flexible backbone

The phase equilibria in block copolymer melts is strongly influenced by the nature of the bond between chemically different blocks. In a weakly associating polymer system macrophase separation prevails, whereas in the case of a covalent bonding the system is restricted to a segregation on a microscopic level, leading to domain structure formation. The intermediate regime, where homogeneous macrophases coexist with microphase separated domains, is particularly interesting and corresponds to the phenomena observed in supramolecular systems. Here we first briefly discuss the covalently bonded comb-like polymers and then address the influence of the thermoreversible bond nature on the equilibrium behavior.

The mean-field WSL approach, similar to that developed by Leibler [105] for the diblock system, can be applied to graft copolymers as well [109–111]. In the case of comb copolymers this was done in particular by Dobrynin and Erukhimovich [110]. In fact, the architecture mainly influences the calculation of the one-chain correlation functions, which, in turn, are used to compute the coefficients in the Landau free energy expansion (for details see [105, 111]). Generally, the correlation functions are obtained assuming Gaussian statistics of the side chains as well as of the backbone pieces between grafting points. This certainly imposes a certain limit on the grafting density and leaves out the bottlebrush-like regime, where the backbone is highly stretched.

In general, the phase diagrams obtained for \((A_n\text{-}\text{graft-B}_m)_k\) polymers are qualitatively similar to those observed in the diblock \(A_nB_m\) case: classical lamellar, cylindrical, and spherical (see Figure 1.5) and complex gyroid structures are found to be stable. However, the critical point shifts to values of the composition \( f = m/(m+n) \) smaller than 1/2, and, thus, in contrast to a diblock, the phase diagram is not mirror-symmetric anymore. Notably, this is a purely architectural effect, which is not present in the analogous phase diagrams of the linear multiblock copolymer \((A_nB_m)_k\).
Supramolecular comb complexes, which appear in mixtures of flexible homopolymers and oligomers able of (hydrogen) bond formation with the monomer units of the polymer [112–115], lead to systems capable of both macro- and microphase separation. The temperature dependence of the hydrogen bond is an utmost important feature of the system. Apparently, a theoretical analysis should include the following three steps. First of all, the statistics of the bond formation should be addressed in order to answer the question about the possibility of comb-like supramolecules formation. Secondly, the homogeneous state has to be analyzed revealing its stability against macro- and microseparation. Finally, in order to build a complete phase diagram, a direct comparison between ordered and homogeneous states has to be performed to calculate their coexistence lines.

A partial analysis, including only the first two steps, was presented by Tanaka and Ishida [116], who showed that microphase separation occurs at near-stoichiometric amounts of polymer and oligomer, whereas an excess of either component gives rise to macrophase separation. This agrees with a more complete picture developed in [117]. The degree of incompatibility of the components, the length of the oligomer chains, and the strength of the reversible bond are the main parameters controlling the stability of the homogeneous state. Going further, Dormidontova and ten Brinke [117] constructed free energies and analyzed stabilities of the classical morphologies. They showed that microphase separation can take place if the tendency to segregate is not very strong and the degree of association is large enough. The larger the incompatibility of the components, the broader the regions of macrophase separation and the smaller the probability to have stable ordered (lamellar or hexagonal) structures in the whole volume of the system.

1.4.2. Phase equilibria in hairy-rod system

The coexistence of homogeneous and ordered phases is typical for the associating polymer system. So, it can be also expected in the supramolecular hairy-rod system, where one of the components (backbone polymer) is a stiff chain [115, 118]. However, systems of this type are much less explored than their flexible counterparts.

Macrophase equilibria in the hairy-rod—solvent and hairy-rod—coils—solvent systems have been studied by Ballauff [119, 120] in the framework of the Flory lattice theory. The primary goal of these works was to describe the nematic phase formation in solution of hairy-rods as well as to address the problem of the compatibility between hairy-rods and high molecular weight solvent (coils) of the same chemical nature as the side chains. Hence, the question about microstructure formation was
completely ignored until now.

A hairy-rod system, in spite of being a close relative to comb copolymers with a flexible backbone, has some distinctive features not encountered in other sorts of comb copolymers. The necessity to incorporate the possibility of liquid crystalline formation in the theoretical modeling can considerably complicate the latter. The presence of a stiff component makes orientational ordering effects an important ingredient of the equilibrium behavior. This also means that application of the relatively simple and well developed WSL or SSL techniques to the hairy-rod system is quite nontrivial.

1.5. Outline of this thesis

In this introductory chapter some relevant experimental results have been presented in order to sketch the questions, potentially interesting for a theoretical consideration, as well as possible applications of the systems based on comb copolymers. We have also outlined the necessary theoretical background for the theory presented further on.

The aim of this thesis is twofold. The first part of it, chapters 2–4, is devoted to single molecule behavior mainly in order to reveal the influence of the side chain properties on the conformational behavior of the comb copolymer. Thus, the elasticity of a comb copolymer molecule with stiff side chains is addressed in chapter 2 and the influence of the attraction between them studied in chapter 3. Next, our attention is turned to a comb-like molecule with chemically different side chains in chapter 4, where the phase separation between chemically different side units is proven to lead to a peculiar bent conformation.

The second objective, pursued in the last two chapters, is related to the phase behavior and self-organization in copolymer melts. In the work presented we develop a theory describing phase equilibria and microstructure formation in a particular type of comb copolymers, “hairy-rods”, characterized by a rigid backbone. In chapter 5 we consider self-organization of covalently bonded hairy-rods, where side chains are attached permanently. Finally, in chapter 6, the more complex problem about phase equilibria in associating rod–coil systems, able of supramolecular hairy-rods formation, is addressed.
Figure 1.1: Examples of polymer architectures: (a) linear polymer, (b) star, (c) comb copolymer "bottlebrush", (d) comb copolymer with rigid side chains, (e) "hairy-rod"

containing typically from hundreds up to tens of thousand units, $N \sim 10^2 - 10^4$, to DNA, where the number of links can reach a billion, $N \sim 10^9$.

It is also possible to obtain *architecturally* more complex branched structures combining linear chains together. The simplest example of such a molecule is a star-polymer, Figure 1.1b, built up from several chemically identical chains. In this thesis we will be mainly interested in another type of branched polymers, so-called comb-shaped polymers: macromolecules, that contain relatively long side branches spaced comparatively closely along the main chain (backbone). Experimentally it is possible to construct such a molecule from chemically identical backbone and side chain units. However, the presence of two types of units – those that form the main chain and those that form the side chains – is a more common property of most