Main Chain Conformation and Anomalous Elution Behavior of Cylindrical Brushes As Revealed by GPC/MALLS, Light Scattering, and SFM‡

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ABSTRACT: High molar mass polymacromonomers based on methacryloyl end-functionalized oligo methacrylates ($M_\text{n} = 2410$ g/mol) adopt the conformation of wormlike cylindrical brushes. Comparison of the absolute molar mass, $M_\text{w}$, determined by static light scattering and the contour length, $L_\text{n}$, of the molecules measured by SFM in the dry state revealed the length per vinylic main chain monomer of the cylindrical structure to be less than 0.1 nm, thus being much shorter than the maximum value of 0.25 nm. In solution this shrinkage could be quantified to 0.071 nm per monomer by Holtzer analysis of the scattering curves which in addition yielded the Kuhn statistical segment length $l_0 = 120$ nm. GPC MALLS investigations of such samples showed an anomalous elution effect: After a regular elution at small elution volumes the molar mass of the eluting molecules increased drastically with increasing elution volume. Fractionation by GPC showed that this effect is caused by a fraction of extremely high molar mass molecules which elute by an unknown mechanism rather than by size exclusion.

Introduction

Polymacromonomers based on polystyrene\textsuperscript{1,2} and poly-(2-vinylpyridine)\textsuperscript{3} side chains and a methacrylate main chain are known to adopt the conformation of cylindrical brushes caused by steric overcrowding of the side chains. Depending on the side chain length, the methacrylate main chain exhibits an extremely high chain stiffness on the order of 100 nm for the Kuhn statistical segment length. In the present paper we report on the preparation and characterization of polymacromonomers with chemically identical main and side chains based on methacrylates which were characterized by GPC/MALLS, by light scattering, and by SFM. Since the successful synthesis of "visible" macromolecules,\textsuperscript{3,7} SFM has advanced to a powerful method not only to image macromolecules but also to determine molecular characteristics such as absolute molar masses, molar mass distribution, and chain conformation, i.e., chain stiffness, complementary to the advanced characterization in solution. In recent papers on poly(vinylpyridine) brushes\textsuperscript{3} and on monodendron jacketed linear chains,\textsuperscript{7} a significant discrepancy was reported between the light scattering molar masses and the molar masses derived from the contour length of the molecules determined by SFM assuming a fully stretched all-trans conformation of the vinylic main chain, i.e., 2.5 Å per monomer unit. To match the light scattering molar masses and the contour length of the cylindrical structure determined by SFM in the dry state, the average repeat length per monomer of the vinylic main chain $l$ had to be significantly reduced to $1.2 \, \text{Å} \leq l \leq 2.3 \, \text{Å}$ depending on the "size" of the dendron as compared to the maximum and commonly adopted value of $l = 2.5 \, \text{Å}$. It was concluded\textsuperscript{7} that the main chain is "locally coiled", but persistent on larger length scales in clear contradiction to Flory's "rotational isomeric state" model which predicts a "length scale independent" decay of the bond vector correlation function. Here we present an investigation on cylindrical brush molecules in solution with particular emphasis on the direct determination of the length per monomer via scattering techniques and compare these results to SFM measurements of the brush molecules in the dry state. We also address the question of whether SFM produces "ensemble average" properties in practice.

Experimental Section

PMMA macromonomers with a methacrylate end group were prepared by group transfer polymerization using a functionalized initiator as described elsewhere.\textsuperscript{6} After purification of the macromonomers by flash chromatography the polymerization was conducted as described earlier:\textsuperscript{2,9,10} 5 g of PMMA macromonomer and 2.5 mg of azobisisobutyronitrile (AIBN) were dissolved in 2.5 mL of benzene and polymerized at 60 °C for 3 days. The macromonomer was purified by precipitation in methanol (which still dissolves the unreacted macromonomer), redissolved in benzene, and freeze-dried. The number-average molar mass of the macromonomer was determined by MALDI-TOF to $M_\text{n} = 2410$ g mol\textsuperscript{-1} as described elsewhere\textsuperscript{8}.

The characterization of the polymacromonomers was performed by size exclusion chromatography equipped with a refractive index detector (Waters 410) and an ALV 1800 multangle light scattering detector (MALLS) operating with an Ar ion laser (514 nm wavelength and 300 mW power) as described elsewhere.\textsuperscript{2,3} The homemade, cylindrical flow cell exhibits a total volume of 36 μL. Size exclusion chromatogra-
Phy was performed in THF utilizing polystyrene gel columns (5 μm, 10^3 Å, 10^5 Å, 10^6 Å nominal pore diameter, PSS Co., Mainz) and a flow rate of 1 mL/min. Typically 100 μL of polymacromonomer (concentration 2–3 g/L) was injected. The shape of the chromatogram did not change for different injected concentrations. Thus, “overloading” of the columns can be excluded.

The fractionation of the PMMA polymacromonomer was achieved by accumulating 75 analytical GPC runs under conditions described above. From each GPC run four fractions were collected with a Gilson FC 205 fraction collector. The THF was evaporated, and the samples were dissolved in benzene and freeze-dried.

The samples for tapping mode SFM measurements were prepared by spin casting (2000 rpm) a dilute solution (c = 0.15 g/L) of the polymacromonomers in chloroform.

Scanning force micrographs were recorded at ambient conditions with a Nanoscope III instrument (Digital Instruments, St. Barbara, CA) operating in the tapping mode. In this mode a cantilever with a sharp tip is oscillated by a piezo driver near its resonance frequency of about 300 kHz. As the tip taps the surface both the amplitude and the phase of the oscillation change, which allows recording of images with a topographic or viscoelastic contrast. The Si probes had a spring constant of about 40 N m⁻¹.

Results and Discussion

In Figure 1 the SFM picture of the methacrylate polymacromonomers reveals a structural similarity to the polystyrene and poly(vinylpyridine) cylindrical brushes. The wormlike nature of the polymer is clearly visualized, and the curvature in terms of the Kuhn statistical segment length of the molecules could principally be analyzed. However, such a procedure does not appear meaningful in order to characterize the intrinsic stiffness as discussed for molecules in solution because (i) the molecules are confined to two dimensions and (ii) the molecular conformation is expected to be susceptible to the interaction with the surface. Moreover, the observed conformation might not even represent an equilibrium state because capillary forces may become dominant during solvent evaporation upon spin casting.

The GPC Anomaly. Following our earlier work on polystyrene polymacromonomers, we utilized our GPC setup with refractive index (RI) and multiangle light scattering (MALLS) detection. In Figure 2 the concentration signal of the eluting molecules reflects the expected broad molar mass distribution along with a tailing toward large elution volumes, which usually would be interpreted as some low molar mass fraction. However, the light scattering signal reveals that at large elution volumes the apparent molar mass of the eluting molecules increases with increasing elution volume in contradiction to the normal size exclusion separation mechanism (see Figure 3). In the following the term “apparent” appreciates the fact that the usual extrapolation of the reduced scattering intensity vs q² might not yield the true molar mass and the true radius of gyration, respectively, because particularly for the large polymers qR_g ≫ 1, which makes zero q extrapolations highly unreliable. This effect is quantitatively addressed in the Appendix and does not alter the qualitative conclusions drawn below from the apparent quantities. Only at small elution volumes is the normal size exclusion behavior observed qualitatively, i.e., decreas-
extremely large. Since light scattering measures the polydispersity of the eluting fractions could become the normally eluting small molecules, thus causing a bimodal molar mass distribution in each fraction of the eluting polymers. Particularly at high elution volumes only very small molecules are expected. Consequently, eluting at large volumes where according to size exclusion mechanisms: the normal size exclusion where the large molecules are retarded, i.e., smaller ones, and an unknown, second separation mechanism where the large molecules are retarded, i.e., elute at large volumes where according to size exclusion only very small molecules are expected. Consequently, a small fraction of extremely large species coelute with the normally eluting small molecules, thus causing a bimodal molar mass distribution in each fraction of the eluting polymers. Particularly at high elution volumes the polydispersity of the eluting fractions could become extremely large. Since light scattering measures the z-average radius of gyration and the weight-average molar mass, the \( R_g - M_w \) curve is shifted upward with increasing polydispersity which qualitatively explains the shape of the curve observed for the unfractionated sample in Figure 4. To prove the above hypothesis, the sample was fractionated as described above. The fractionation cutoffs are marked by arrows in Figure 2.

The explanation for GPC anomaly as discussed above is qualitatively confirmed by the static and dynamic light scattering results shown in Figure 5. Fractions 2 and 3 exhibit correlation functions which display a monomodal decay with moderate polydispersity (normalized second cumulant \( 0.08 \leq \mu_2 \leq 0.1 \)), yielding hydrodynamic radii of \( R_h = 50 \text{ nm} \) and \( R_h = 38 \text{ nm} \), respectively. In contrast, the correlation functions of fraction 4 show a bimodal decay. The slower decay constant corresponds to a hydrodynamic radius of \( R_h \approx 120 \text{ nm} \), and the fast decay yields \( R_h = 19 \text{ nm} \). For the correlation functions of fraction 1 a bimodal decay cannot be convincingly postulated. Whereas the apparent diffusion coefficients \( D_{app} = 1/q^2 \) depend only slightly on the scattering angle for fractions 2 and 3, a strong dependence was observed for fraction 1 (a factor of 2 from \( 0^\circ \) to \( 130^\circ \) scattering angle). This may indicate a larger polydispersity of the sample which is also indicated by somewhat larger values of \( \mu_2 = 0.10 \text{–} 0.12 \). It is also conceivable that extremely large molecules may be filtered out or break during filtration. A more detailed investigation of such subtle effects was prohibited by the extremely small amount of sample available (~1 mg).

Likewise, the static light scattering results exhibited unusually high uncertainties due to the weighing error. Eventually the concentration was determined via GPC by comparing the peak area of the refractive index signal of the light scattering samples to the peak area of linear PMMA of known concentration. Due to the small signals obtained, the concentration determination is accurate to ±20%, only. At the small concentrations investigated \( (c > 0.1 \text{ g/L}) \) this does not seriously affect the apparent radius of gyration, but rather the apparent molar mass. As will be discussed below in detail, also

\[
\langle S^2 \rangle_z = \frac{\langle R^2 \rangle_{app} - \langle R \rangle_{app}^2}{\langle R \rangle_{app}}
\]
the extrapolation to zero q is highly ambiguous because of the large u = qR \_g values reached by the present samples. Even at 15° scattering angle u becomes larger than 1 for fractions 1 and 4, which makes a reliable extrapolation for the determination of M \_w and R \_g impossible. Therefore, we give a crude estimate of the molar masses of fractions 1 and 4 based on the hydrodynamic radii, because these are insensitive to incorrect concentrations and do not suffer strongly from zero q extrapolation problems. The statistic and dynamic light scattering results are summarized in Table 1. From the above results the GPC anomaly is qualitatively explained. It is, however, extremely difficult to trace the origin of the anomalously eluting large molecules. The obvious explanations comprise overloading of the columns, adsorption, and sieving. Overloading of the columns can be safely excluded, because the shape of the elution peak did not change upon reduction of the injected amount of sample by more than a factor of 10. Retardation by adsorption of the molecules onto the column material seems to be unlikely, because THF can hardly adsorb onto the high molar mass species. For large column material, however, should provide an effective separation which represents the column material. Such a mechanism, however, should provide an effective separation which seems not to be compatible with the similar radii observed for fraction 1 and for the high molar mass component in fraction 4. It should be noted that the anomalous elution described above is not unique to the fraction 1 components, but is observed for fraction 1 and for the high molar mass species of the bimodal chain length distribution established by dynamic light scattering.

\[ M \_w^{\text{app}} = 10^6 \text{g mol}^{-1} \]

\[ R \_g^{\text{app}}/\text{nm} \]

\[ R \_n/\text{nm} \]

\[ L \_w^{\text{SFM}}/\text{nm} \]

\[ L \_n^{\text{SFM}}/\text{nm} \]

\[ l \_\text{SFM}/\text{nm} \]

\[ F \]

\[ \approx 60\text{°} \]

\[ 170 \]

\[ 103 \]

\[ 640 \]

\[ 485 \]

\[ 0.026 \]

\[ F \]

\[ 14 \]

\[ 84 \]

\[ 50 \]

\[ 443 \]

\[ 322 \]

\[ 0.076 \]

\[ F \]

\[ 7.5 \]

\[ 70 \]

\[ 38 \]

\[ 254 \]

\[ 193 \]

\[ 0.081 \]

\[ F \text{ (comp 1)} \]

\[ 1.7 \]

\[ 119 \]

\[ 72 \]

\[ 49 \]

\[ 0.1 \]

\[ F \text{ (comp 2)} \]

\[ 100\text{°} \]

\[ 120 \]

\[ a \] Fraction 4 contains a low (comp 1) and a high molar mass component (comp 2).

\[ b \] Estimated from the hydrodynamic radius.

\[ c \] Length per monomer according to \( L \_w^{\text{SFM}} M \_w M \_w^{\text{app}} \).

**SFM Characterization of the Fractions.** To compare the light scattering molar masses to the contour length of the cylindrical brush molecules, the four fractions were investigated by SFM as shown in Figure 6a–d. On a small scale inspection of the SFM pictures does not reveal an obvious reason for the anomalous elution behavior of the fractions; i.e., no bimodal distribution of the contour length is observed for fraction 4 in contradiction to the dynamic light scattering results discussed above. In Table 1 the light scattering molar masses of the fractions are compared to the contour lengths extracted from the SFM pictures which yields the length per monomer \( l \_\text{SFM} \) via the known mass \( M \_0 = 2410 \text{ g mol}^{-1} \) of the macromonomer.

\[ l \_\text{SFM} = L \_w^{\text{SFM}} M \_0 M \_w^{\text{app}} \]

The results for \( l \_\text{SFM} \) lie in the range \( 0.076 \text{ nm} \leq l \_\text{SFM} \leq 0.1 \text{ nm} \) for fractions 2, 3, and 4. For fraction 1 SFM obviously misses some large molecules which is caused either by the statistical inaccuracy, i.e., the limited number of monitored molecules as compared to the broad length distribution, or by fractionation during spin casting. This effect becomes even more pronounced for fraction 4 where the high molar mass species of the bimodal chain length distribution established by dynamic light scattering is completely absent in the SFM picture shown in Figure 6d. Under the assumption that the missing molecules exhibit a similar or larger molar mass than those of fraction 1, the number fraction of large species in fraction 4 is estimated to be certainly less than \( 10^{-3} \). Thus, it might be a problem for SFM to detect an extremely small number fraction of high molar mass species due to the limited number of molecules observed. Indeed, a careful inspection of large-scale micrographs of fraction 4 reveals that very few “monolayer islands” do exist (see Figure 6e) which are composed of extremely large molecules as shown in Figure 6f. Qualitatively, this observation impressingly confirms the proposed bimodal distribution of fraction 4.

This example demonstrates that monitoring “ensemble averages” by SFM may suffer significantly by the limitation in the statistical accuracy and possibly by fractionation during sample preparation, i.e., spin casting. For the monomodal fractions 2 and 3 comparison of the light scattering molar masses and the SFM contour length yields a length per monomer \( l \_\text{SFM} = 0.07–0.1 \text{ nm} \) in qualitative agreement with the results obtained for poly(vinylylpyridine) brushes and for monodendron jacketed polymers. A similar conclusion is drawn from the cross-sectional dimensions of the brushes observed by SFM which were determined to a brush height \( h = 4.7 \pm 0.2 \text{ nm} \) and a width of \( d = 11 \pm 1 \text{ nm} \). Assuming the density of a dry brush molecule to be identical to the bulk density of PMMA, \( \rho \_\text{PMMA} = 1.19 \)
g/cm³, the length per monomer is calculated to \( l_\theta = 0.084 \pm 0.01 \) nm where an ellipsoidal cross section of the molecules is calculated according to \( F = \pi h d/4 \). Within experimental error \( l_{\text{SFM}} \) and \( l_\theta \) both determined in the
The discussion of the curve at $V_L$ curves correspond to molecules eluting at different volumes by GPC/MALLS of the unfractionated sample. The different Figure 7.  

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which principally allows the determination of MALLS data in terms of the well-known Holtzer plateau following discussion. 

4 is so strange that these data are excluded from the 

sion above. Particularly the elution behavior of fraction 

more or less anomalously as expected from the discus-

sionated and of the unfractionated samples can be 

utilized for the precise analysis of the particle scattering 

factor. Therefore, additional GPC/MALLS measure-

ments were performed on fractions 1–4, the results of 

which are included in Figures 3 and 4. All fractions elute 

more or less anomalously as expected from the discus-

sion above. Particularly the elution behavior of fraction 

4 is so strange that these data are excluded from the 

following discussion. 

We now analyze the scattering envelopes of the GPC/ 

MALLS data in terms of the well-known Holtzer plateau 

which principally allows the determination of $M_L$ and $I_k$. This is shown in Figure 7 for the data of some GPC 

slices of the unfractionated sample, where $qR_g/Kc$ is plotted versus the apparent quantity $u_{app} = qR_{app}$. At 

small elution volumes, i.e., high molar masses, the data exhibit a pronounced maximum typical for semiflexible 

polymers whereas at large elution volume, i.e., small 

molar masses, a monotonically increasing curve is 

observed which levels off at a constant value at high $q$. 

This is the well-known Holtzer plateau $\pi M_L$ which 

allows the determination of the length per monomer via 

the known mass per repeating unit $M_0$. 

\[ I = M_L/M_0 \] 

From Figure 7 we derive $M_L = 33 400$. The data of 

fractions 1–3 yield similar results with values of $M_L = 34 000 \pm 5\%$ corresponding to $I = 0.071$ nm. This value 

agrees well with $I_k$ and $I_{SFM}$ determined in the dry state (see Table 1). So far the length per monomer could 

be derived without the detailed model calculation of the particle scattering factor. We merely had to confine 

ourselves to the analysis of those data that belong to 

the normally eluting part of the chromatogram. "Nor-

mally eluting" means that the chain length distribution 

within a single elution slice of 0.06 mL is monomodal 

with a polydispersity $M_u/M_o < 2$. It will be shown in 

the Appendix that for bimodal chain length distributions 

of extremely large polydispersity too small values of the 

Holtzer plateau may be experimentally observed. For the data in the anomalous elution regime this is 

experimentally confirmed as shown by the solid circles 

in Figure 7.

At present the origin of the observed small length per 

monomer is difficult to discuss. Certainly a helix forma-

tion would lead to a smaller contour length. This would 

require the main chain to exhibit a pronounced tacticity 

which could not be detected by high-resolution NMR. 

Alternatively, the steric overcrowding of the side chains 

could force the main chain into well-defined gauche/ 

trans sequences, which, however, are not likely to lead 

to a perfect helix. For monodendron jacketed polymers 

the solid-state structure was proven by elaborate X-ray 

diffraction experiments to consist of helical arrange-

ments of the side chains, however, with no detectable 

order of the main chain. 

Therefore, the reduced contour length for the monodendron jacketed polymers was explained by a "random helix formation". 

In view of simulations and scaling arguments on flexible polyelectrolytes claiming a persistent arrangement of locally coiled segments ("Gaussian blobs"), a similar scenario could be constructed for the cylindrical brushes as well. In fact, recent Monte Carlo simulations of cylindrical brush molecules demonstrate the bond angle correlation function to exhibit two decay constants which, however, were not evaluated in a systematic 

manner. In the present state of investigation a quanti-

tative comparison with the experiments is not mean-

ingful, because the intrinsic stiffness, i.e., unperturbed 

Kuhn length, is not accounted for in the Monte Carlo 

simulations. As a consequence, the MC simulations 

observe a much smaller increase of the persistence 

length of the main chain, if the size of main and side 

chain monomers are identical, in clear disagreement 

with the experimental results. The problem of the 

reduced contour length for polymacromonomers has not 

yet been addressed directly by theory or simulations but 

becomes qualitatively evident from pictures of simulated 

structures. 

We currently believe that no regular, 

i.e., helical, structure of the main chain is required in 

order to induce the cylindrical structure of the brush 

molecules. Rather, the steric interaction of the side 

chain may straighten out locally coiled segments which 

might not at all exhibit a significant helicity.

Determination of the Chain Stiffness. A precise 

analysis of the shape of the scattering curves principally 

allows the determination of the “true” radius of gyration, 

the Kuhn statistical segment length, and the polydis-

ersity within a single elution slice. However, there are 

three major obstacles to overcome: (i) Due to the scatter 

of the experimental data, a fit with model calculations 

for the particle scattering factor might not be unique. 

In the present problem this ambiguity is significantly 

reduced because one set of parameters should fit several 

scattering curves. (ii) Since the molar mass distribution 

within a single elution slice is unknown, we have to 

assume a chain length distribution function in the model 

calculation. Here we have utilized a Schulz–Zimm 

distribution with variable convolution parameter $m$. (iii) 

The particle scattering factor for semiflexible polymers
of finite length is not yet precisely known. We adopt the approximate model introduced by Koyama\(^{29}\) which was successfully employed in earlier investigations.\(^{30,31}\)

To practically start with the theoretical modeling of the scattering curve, we have to introduce a better estimate for the quantity \(u\) instead of \(u_{\text{app}}\). This is crudely achieved (\(\pm 10\%\)) by rescaling \(u_{\text{app}}\) in Figure 8 such that the maximum of the curves is located at \(u = 1.55\), because model calculations have shown the maximum to shift from \(u = 1.4\) for monodisperse \((m = \infty)\) to \(u = 1.7\) for Schulz–Flory distributed samples \((m = 1)\).\(^{31}\)

The next step involves a direct comparison of the theoretical to the experimental curves. The height of the scattering curve, we have to introduce a better convolution parameter \(m\) also determines the precise position of the maximum, the true radius of gyration is easily evaluated once \(m\) is known. The result is shown in Figure 8, where the normalized curves \(\tilde{q}P(q)\times L_{w/\ell} = qR_{\tilde{g}}(K_{d}M_{c}/\tau)\) are plotted vs \(u = qR_{\tilde{g}}\) with \(R_{\tilde{g}}\) the radius of gyration derived from the position of the maximum at fixed (and at least approximately known) convolution parameter \(m\). The coincidence of experimental data and theoretical curves is almost perfect in view of the fact that deviations are magnified in the Holtzer plot. In practice, it was sufficient to create three sets of theoretical curves with \(m = \infty\), \(m = 8\), and \(m = 4\) corresponding to \(M_{w}/M_{n} = 1.0, 1.125\), and 1.25, respectively, each consisting of 20 \(L_{w}/\ell_{k}\) values between 0.1 and 15.

The resulting values for \(L_{w}/\ell_{k}\) and \(R_{\tilde{g}}\) obtained by comparison of the experimental to the theoretical curves are listed in Table 2 for selected elution slices of the unfraccionated sample and of fractions 1–3.

The next step involves the determination of \(L_{w}\) and \(\ell_{k}\) at given \(L_{w}/\ell_{k}\) and \(R_{\tilde{g}}\) values. The quantity \(u\) is more voluminous than the methacrylate monomer. This is simply explained by the fact that in the earlier investigation\(^{2}\) the contour length was derived utilizing the 

\[
R_{g}^{2} = \frac{m + 2}{6y} + \frac{l_{k}^{2}}{4} + \frac{y^{2}}{4(m + 1)} - \frac{l_{k}^{m+2}}{8m(m + 1)} - \frac{y^{m+2}}{(y + 2\ell_{k}^{m})^{2}}
\]

with \(y = (m + 1)/L_{w}\). Then \(L_{w}\) and \(\ell_{k}\) were varied at fixed \(L_{w}/\ell_{k}\) and \(m\) until the calculated radius of gyration, \(R_{g}^{2}\), is equal to \(R_{\tilde{g}}^{2}\). This procedure consistently yields \(\ell_{k} = 120\) nm. Only for the smallest molar masses in each of the samples which are close to the anomalous elution regime are large deviations of \(R_{g}\) and \(R_{\tilde{g}}\) observed which are marked by stars in the first column of Table 2.

As shown in the Appendix, these deviations are most probably caused by the onset of anomalous elution, i.e., the occurrence of a bimodal chain length distribution within a single elution slice. We now utilize the values of the contour length and the mass per unit length \(M_{w}\) in order to calculate the true molar mass of the eluting molecules, which is also included in Table 2. Comparison of the true with the apparent quantities reveal huge differences of up to 30% and 40% for \(M_{w}\) and \(R_{\tilde{g}}\), respectively, despite the apparent linearity of the experimental Zimm plots. To elucidate these subtle effects, three of the data sets shown in Figure 8 were replotted as \(P(q)^{-1}\) vs \(u^{2}\). In Figure 9 the solid line represents the wormlike chain fit whereas the broken line shows the linear regression. In fact, the linear regression is seen to be hardly worse than the wormlike chain fit but yields extremely wrong \(M_{w}\) and \(R_{g}\) values for the high molar mass samples. In the anomalous elution regime the calculated \(M_{w}^{c}\) becomes wrong because \(L_{w}/\ell_{k}\) is too small as outlined in the Appendix. For this reason \(M_{w}^{\text{app}}\) and \(M_{w}^{c}\) almost never agree.

The quantitative value for the chain stiffness \(\ell_{k} = 120\) nm is significantly larger than determined for polymacromonomers with polystyrene side chains of similar length, which is counterintuitive because the styrene is more voluminous than the methacrylate monomer. This is simply explained by the fact that in the earlier investigation\(^{2}\) the contour length was derived utilizing a length per monomer of \(l = 0.25\) nm. Accordingly, the values reported earlier represent the lower limit of the chain stiffness.

Conclusion

Polymacromonomers consisting of methacryloyl end-functionalized oligomethacrylates exhibit a cylindrical structure that is characterized by an enormously high chain stiffness, i.e., \(\ell_{k} = 120\) nm. This stiffening is caused solely by steric overcrowding of the densely packed side chains. The incompatibility of main and side chains in earlier investigated polymacromonomers with a polymethacrylate main chain and polystyrene side chains\(^{1,2}\) does not have a significant influence on the chain stiffness.

For the first time the length per monomer of the cylindrical brush molecules has been determined in solution to \(l = 0.071\) nm, which is much smaller than the maximum value of \(l = 0.25\) nm for vinylic main chains. The contour length of the molecules in the dry state observed by AFM yields similarly small values for \(l\), thus confirming earlier observations on poly(vinylpyridine) brushes\(^{3}\) and on monodendron jacketed linear chains.\(^{7}\) This allows the important conclusion that the reduction of the contour length as compared to its maximum value does not occur during the drying process in the first place but exists in solution as well. The limitations of SFM to monitor ensemble properties for samples exhibiting a very broad chain length distribution and the inaccuracy of the light scattering results, if only sub-milligram amounts of sample are...
available, prohibit a more quantitative comparison of the contour length of the cylindrical brushes in the dry and dissolved state. Accordingly, future investigations will focus on more perfect fractionations, i.e., obtain a larger amount of sample with a significantly reduced polydispersity of the chain length.

The anomalous elution of high molar mass polymacromonomers has been detected by GPC/MALLS and could be reduced to a delayed elution of an extremely high molar mass fraction of the sample. The origin of the retardation, however, remains unclear.

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Appendix

To investigate the effect of a bimodal chain length distribution in the Holtzer plot, two model calculations are performed. In Figure 10a the Holtzer plots for two monodisperse wormlike chains of \( L_1/l_k = 10 \) and \( L_2/l_k = 1 \) are shown together with the curve for the mixture of both with identical mass fractions \( m_1 = m_2 = 0.5 \). The solid line represents the best fit to the mixture utilizing the theoretical calculation of the form factor.
with a monomodal Schufl – Zimm chain length distribution. The fit parameters are $L_w/L_k = 3.3$ and $m = 3$ (yielding $L_w/L_n = 1.33$) which ought to be compared to the true values $L_w/L_k = 5.5$ and $L_w/L_n = 3$. The fitted contour length $L_w$ is clearly too small, which perfectly explains the discrepancy between the $R_s^0$ and $R_m^0$ values observed at higher elution volumes listed in Table 2 in the text.

The second calculation addresses the experimental results obtained in the regime of anomalous elution, one example of which is included in Figure 7. Here, the chain length distribution is expected to be bimodal with extremely large polydispersities. Therefore, in Figure 10b the Holtzer plot of two monodisperse samples with $L_w/L_k = 10$ and $L_w/L_k = 0.1$ are shown together with the scattering curve for the mixture with mass fraction $m_1 = 0.01$. Within the experimentally accessible regime the Holtzer plateau is never reached. Both examples clearly impose strong limitations to the applicability of the data analysis proposed above. It should be noted, however, that the apparent Holtzer plateau obtained for extremely bimodal distributions would lead to unphysically small $M_L$ values, i.e., too large $l$ values.

References and Notes


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