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Indenting polymer brushes of varying grafting density in a viscous fluid: A gradient approach to understanding fluid confinement

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HIGHLIGHTS

- Poly(dodecylmethacrylate) brushes with varying grafting densities were created via UV cleaving.
- A recently developed colloidal-probe nanoindentation approach was used to study fluid confinement.
- Contact modulus below 1 kPa was measured for all grafting densities in hexadecane.
- Liquid squeeze-out ahead of contact appears to be independent of grafting density.
- Higher grafting densities showed more fluid confinement within the polymer layer.

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ABSTRACT

A sound understanding of the fluid-confinement mechanics of soft materials, including polymer brushes or hydrogels, is essential for developing advanced biomedical and engineering applications such as contact lenses or low-friction coatings. In order to elucidate the effect of polymer-chain density on fluid confinement in thin films, gradients of poly(dodecyl methacrylate) (P12MA) brushes with varying grafting densities were created via a UV-cleaving process and studied using colloidal-probe atomic force microscopy (CP-AFM) nanoindentation. A recently developed indentation methodology that accounts for viscous squeeze-out effects upon approach allowed for the accurate determination of the properties of the soft, thin materials. The indentation of different grafting densities of brushes of identical molecular weights solvated by a common viscous liquid (i.e. hexadecane) allowed direct comparison of rate-dependent fluid confinement within thin surface-grafted polymer layers. This revealed comparable mechanical properties upon quasi-static indentation for the different grafting-density polymer brushes, showing an elastic modulus of about 0.3 kPa in the topmost part of all layers. At nonfinite rates of indentation, the higher grafting densities showed more fluid confinement. The insight gained opens new possibilities for soft thin-layer characterization and provides an accessible technical approach to studying fluid confinement.

1. Introduction

Polymer brushes share some common architectural, mechanical, and friction-reduction properties with natural materials, such as the proteoglycans in articular cartilage and glycoproteins in mucus [1–5]. Measurements on cartilage have shown that reduced density of proteoglycans—an effect frequently observed in patients diagnosed with osteoarthritis—can lead to loss of fluid-load-support-related mechanical properties [6]. The dependence of fluid confinement on proteoglycan density has inspired us to study the effects of varying grafting density of polymer brushes on their confinement of solvent. The ability to confine liquid (e.g. water or synovial fluid) is frequently associated with chemical or physical interactions between the brush and the fluid, enabling fluid-load support and preventing direct contact between brush-coated surfaces [7–11]. This property can also be exploited in tribological applications for extending the boundary-lubrication regime [12–15]. Such behaviour is not limited to aqueous systems, and similar effects can also be observed in oil-compatible polymer brushes. Recent

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experiments on poly(dodecylmethacrylate) (P12MA) brushes showed the brushes’ ability to Confine the solvent, extend the mixed-lubrication regime and thus delay the onset of boundary friction [16–18]. Espinosa et al. [19] have performed indentation experiments on P12MA in various solvents using the extended surface forces apparatus (eSFA) [20,21], revealing a viscosity dependence of the confinement of fluid during contact.

Besides SFA, atomic force microscopy is also a powerful technique to study thin films, not only in terms of the characterization of topography, but also with respect to the measurement of local materials properties, including elasticity, hardness and adhesion [21]. Specifically, colloidal-probe atomic force microscopy (CP-AFM) nanoindentation has become a standard technique for probing soft matter [22–25]. CP-AFM nanoindentation allows for a wider range of substrates to be tested than the surface forces apparatus and is also more flexible in terms of indent geometries and cantilever stabilities compared to conventional nanoindentation setups [26–28]. Independent of the instrument used, the determination of the contact point in the force-separation curves obtained in indentation of soft matter remains a challenging issue [26,27,29–32]. The problem is magnified at non-finite indentation rates and viscous solvents, since upon approach, viscous fluids can be confined between the probe and sample surface, resulting in an increase in the force experienced by the probe ahead of the actual contact [33]. Therefore, determining the contact point during rate-dependent indentation can be especially difficult for polymer brushes in viscous good solvents—a system of particular interest for lubrication [34,35].

Targeting this major issue in soft-matter-indentation measurements, we employ a recently developed method to identify the point of contact between a probe and a polymer-brush layer in a viscous environment upon rate-dependent indentation [36]. Once the point of contact is unambiguously ascertained for non-finite rates, viscous drag and squeeze-out effects can be subtracted and the rate-dependent mechanical properties of varying-grafting-density brushes can be determined. Understanding the biphasic properties of soft permeable materials is essential in the development of synthetic replacement materials for cartilage and provides new insights into many related biomedical and engineering applications.

2. Experimental

2.1. P12MA grafting-density gradient fabrication

In order to fabricate poly(dodecylmethacrylate) (P12MA) brushes of varying grafting density on silicon substrates, a photo-cleavable surface-initiated, atom-transfer radical polymerization (SI-ATRP) initiator was first synthesized according to our previously described method [37,38]. After deposition of the initiator, P12MA brushes were subsequently grown from the substrate by SI-ATRP [39]. Because P12MA brushes were attached to the silicon substrates via a photo-cleavable linker incorporated within the SI-ATRP initiator, P12MA chains could be detached by exposing the sample to UV light with a wavelength of 366 nm, which is too long in wavelength to attack the polymer chains themselves [37]. Given the simple, first-order kinetics of this reaction, the number of chains removed could be readily controlled by adjusting the irradiation time [39]. In this way, a step-gradient with three distinct grafting-density domains could be fabricated on a single silicon substrate using a shutter to control the UV exposure time on different parts of the wafer. The UV-induced detachment of P12MA chains from the substrate resulted in a decrease in the grafting density of the remaining P12MA layer, which could be measured as a reduction in dry, collapsed thickness. The dry thickness of the polymer layers was determined by spectroscopic ellipsometry (M200-P J.A. Woollam Co. Inc., Lincoln, USA) over a spectral range from 370 nm to 995 nm. The spectrum was fitted using a model that consisted of a pure silicon substrate, a thin Si-oxide layer and a Cauchy layer of refractive index 1.45 on top. The VWASE 32 software provided with the instrument was used for the fitting. An average value of thickness from at least three measurement points was used and the standard deviation reported to one significant digit.

2.2. Molecular-weight evaluation

To determine their number-averaged molecular weight, as well as their polydispersity, the polymer brushes were detached and gathered from the same planar substrate the gradient sample is fabricated from, using the previously reported photocleavage procedure [37]. The gradient domains are prepared using a shutter and exposing a specific area of the photo-cleavable polymer brushes to a defined dosage of UV irradiation. With increasing dosage, increasing amounts of polymer chains are cleaved from a domain, resulting in varying grafting-density domains. A number-averaged molecular mass Mn of 371.4 kDa (g/mol) and a polydispersity index (PDI) of 1.5 were obtained via a Viscotek Size-Exclusive Chromatography SEC system equipped with a pump, a degasser (SEC Max VE2001), a detector module (Viscotek 302 TDA), a refractive-index (RI) detector and two columns (PLGel Mix-B, PLGel Mix-C). Chloroform was used as an eluent with a flow rate of 1.0 mL/min. Molecular weight of P12MA was measured using a universal calibration method in which the product of the logarithm of the intrinsic viscosity η multiplied by the molecular weight M or ln(Μ) is plotted against the retention volume, with polymeric standards in the range of Mw 1480–4340000 Da. Rudin and Hoey have shown that such a calibration method is extremely effective in determining true molecular weight of a polymer when the concentration of the polymer solution is taken into account [40,41].

2.3. Grafting-density variation

To calculate the surface coverage in units of g/m², the dry polymer thickness t (m) was measured via ellipsometry. Assuming a density ρ (g/m³), the surface coverage Γ (g/m²) is:

\[ \Gamma (h) = \rho t \]  

where the density ρ was assumed to be 0.897 × 10⁶ g/m³ in a dry state, as reported by Zhao et al. [42]. Knowing the surface coverage, the grafting density Σ (number of polymer chains per m²) can be obtained as:

\[ \Sigma (t) = \frac{\Gamma N_A}{M_c} \]  

where M_c is the number-averaged molecular mass and N_A is Avogadro’s number. Assuming hexagonal packing of the initiators, the mean separation D (m) between adjacent polymer chains can be calculated as:

\[ D (t) = \sqrt{\frac{2}{\Sigma (t) \sqrt{3}}} \]  

A summary of the properties of each thickness domain on the polymer-brush gradient is listed in Table 1. By means of the UV-induced cleavage, we could reduce the number of chains on the surface, thus increasing their anchor spacing and thereby reducing surface coverage and grafting density. We divided the sample into three regions of low

| Table 1 |
|-----------------|-------|------|-----|
| Dry thickness t (nm) | 20.3 ± 1.0 | 113.9 ± 0.2 | 159.8 ± 0.7 |
| Surface coverage Γ (mg/ m²) | 18.2 ± 0.9 | 102.2 ± 0.2 | 143.3 ± 0.6 |
| Grafting-density Σ (chains/ nm²) | 0.030 ± 0.001 | 0.166 ± 0.003 | 0.232 ± 0.001 |
| Chain spacing D (nm) | 6.25 ± 0.30 | 2.64 ± 0.01 | 2.23 ± 0.01 |
Table 2
Contact configurations yielding a Péclet number of 1 when testing a P12MA brush in hexadecane using three different experimental devices.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>( R ) (( \mu \text{m} ))</th>
<th>( \nu ) (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Forces Apparatus</td>
<td>20000</td>
<td>2(^{\circ} )</td>
</tr>
<tr>
<td>Nanoindenter</td>
<td>500</td>
<td>80(^{\circ} )</td>
</tr>
<tr>
<td>AFM-indentation</td>
<td>40</td>
<td>1000</td>
</tr>
</tbody>
</table>

* An estimation of the rate at the onset of fluid-load support was made on the basis of results published in Ref. [19].

The probe radius \( R \) and indentation rate \( \nu \) of the AFM-nanoindentation experiments were chosen to achieve a similar advective transport rate to those of earlier surface-force-apparatus (SFA) and nanoindentation experiments conducted on a P12MA brush grafted from mica surfaces and tested in hexadecane [19]. Assuming indentation of the identical material, Table 2 shows how three different experimental setups can provide comparable contact configurations reaching a Péclet number of 1. Characteristic of Péclet numbers above 1, earlier experiments showed fluid-load support when performing SFA measurements using a probe of radius 20 \( \mu \text{m} \) at a rate above 2 \( \text{nm/s} \). Similar experiments performed with a nanoindenter setup with a sphere of 500 \( \mu \text{m} \) radius at rates above 80 \( \text{nm/s} \) also showed that a fluid-load-support contribution was evident.

By changing the AFM indentation rates between 200 and 2000 \( \text{nm/s} \) and using a 40 \( \mu \text{m} \) radius spherical probe, we therefore expected to be able to test the material under both low and high Pe regimes. An MFP-3D AFM (Oxford Instruments, Asylum Research, Santa Barbara, CA, USA) was used to perform the displacement-controlled, colloidal-probe AFM nano-indentation experiments in this work. The experiments were performed on the previously described gradient samples, fully immersed in hexadecane, after equilibrating the experimental setup for at least 15 min. AFM probes were produced by gluing silica spheres (Kromasil, Brewster, NY, USA) of 40 \( \mu \text{m} \) radius onto tip-less cantilevers (u-masch, San Jose, CA, USA) of 0.29 N/m spring constant using an in-house micromanipulation setup [48]. The cantilever normal spring constants were calibrated using the thermal noise method [49]. The normal sensitivity of each probe was determined by measuring the slope of the deflection vs. \( z \)-piezo displacement curve obtained on a silicon surface in the relevant solvent.

For the indentation experiments, the approach rates were varied as mentioned earlier. After reaching a maximum applied force, a piezo-displacement-controlled equilibration period of 1 s followed, which was sufficient to reach complete relaxation. Finally, retraction of the probe with the same rate of indentation was performed. A schematic of the indentation protocol is depicted in Fig. 1 below. Each indentation experiment was performed at least ten times to guarantee reproducibility.

Using the information on the point of contact, one can evaluate the force-indentation curves using classical contact mechanics. For small indentation depths the well-known Sneddon model reduces to a classical Hertzian model, described by Equation (5) [34,50]. Knowing the probe radius \( R \) and assuming a Poisson’s ratio \( \nu \) of 0.5, the elastic modulus \( E \) can be calculated from the force \( F \) experienced by the probe at increasing indentation depths \( \delta \) [51].
3. Results and discussion

3.1. Contact-point determination

To accurately determine the point of contact between a probe and a soft material surface in presence of a viscous fluid an indentation methodology recently presented by Simic et al. for bulk hydrogels was used on the polymer-brush layers [36]. Fig. 2 illustrates how the indentation methodology was adapted to indentation on highly viscous P12MA thin-films. For the slowest indentation rate of 0.2 \( \mu m/s \) only negligible viscous drag and squeeze-out forces were assumed, and the contact point was determined at a probe position, where the normal force upon the approach is no longer within one standard deviation (\( \approx 0.075 \) nN) from the average determined far away from the surface (threshold method). For all the faster-rate indentations, however, the viscous squeeze-out ahead of contact was substantial. In these cases, the approach and the retraction curves far from the surface were assumed to be symmetrical about zero force and therefore a linear function was fitted to the average of the approach and retraction curves far from the contact. The fitted linear function was then subtracted from the entire curve to remove the background slope, see Fig. 3.

The indentation part of the slow indentation curve was then fitted using \( F = \frac{4}{3} R^{0.5} E \left( 1 - \nu^2 \right)^{1.5} \delta^{3.5} \), which best described the force-distance curve. Due to a small amount of force relaxation observed after reaching the set-point even at the slowest rate, the same shape of a curve \( F = K \exp (n \delta) - 1 \) was fitted through the relaxed point assuming a linear contribution of the confinement to the force with increasing indentation depth. The obtained curve was assumed to show a purely elastic response of the brush that would be observed at an infinitely slow indentation rate and was therefore used for the depth-alignment of the relaxation points from the force curves obtained at all the faster rates, Fig. 4. Thus, the relaxation points of the faster rates should coincide with the curve showing purely elastic response, as discussed by Simic et al. [36] Similarly, Charrault et al. recently reported that for infinitely slow indentation rates, only the elastic contribution, and thus an equilibrium elastic modulus, is measured on a force-indentation curve when indenting polymer brushes in the presence of a good solvent—a system characterized by both porous and viscoelastic properties [35].

Fig. 3 shows already aligned force-indentation and retraction curves for HD-, MD- and LD-P12MA for 0.2, 0.5, 1 and 2 \( \mu m/s \) indentation rates. From the data shown in Fig. 3 it is apparent that the force offset at zero indentation is increasing upon increasing the rate of indentation for all grafting densities.

Up on magnification of the force vs. indentation curves for HD-/MD-/LD-P12MA, see Fig. 4 a, b, c respectively, collected at different indentation rates, a stiffening response of the material upon increased indentation rate is evident. For indentation rates of 0.5 \( \mu m/s \), 1 \( \mu m/s \) and 2 \( \mu m/s \) the alignment of the relaxation points to the red line allowed us to trace back the point of intersection of the curve at zero-indentation, i.e. the point of contact.

In Fig. 5, the force offset at the point of contact due to the viscous squeeze-out effects ahead of contact is shown for the different indentation rates. By knowing the deflection and z-sensor position, the actual indentation velocity of the probe can be calculated at the point of contact and are reported as such in the figure. The contact-force offset increased with indentation rate, as expected due to the presence of viscous dissipation [52,53]. Moreover, it can be seen that the force offset increases almost linearly with increasing indentation rate, as predicted by Vinogradova et al. [54] A deviation from the linear behaviour could also be caused by a slight deformation of the soft layer during the approach [4,55].

\[
F(\delta) = \frac{4}{3} R^{0.5} E \left( 1 - \nu^2 \right)^{1.5} \delta^{3.5}
\]  

(5)
3.2. Mechanical characterization of varying grafting-density polymer brushes

From AFM nanoindentation experiments performed on the LD-, MD- and HD-P12MA in hexadecane, swollen thicknesses in hexadecane of at least 245 nm, 339 nm and 490 nm, respectively, were estimated (Fig. 4). Assuming that under the highest applied load the swollen brush was compressed all the way down to its dry thickness, the lower limit of the

Fig. 4. Average force indentation curves for a) HD-P12MA b) MD-P12MA c) LD-P12MA indented at different indentation rates. In red the fitted “zero-rate” indentation curve is indicated. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
swollen thickness could be determined by adding the total indentation depth to the dry thickness. Comparing these values to the dry thickness evaluated via ellipsometry, this implies a minimum swelling ratio of about 12, 3 and 3 for LD-, MD- and HD-P12MA, respectively. Theoretical calculations (see Supplementary Material) support the minimum swelling ratios, and from the critical grafting-density as well as the crowding threshold, a densely packed brush-structure is expected for HD-P12MA and MD-P12MA, while for LD-P12MA individual chains have ample space, adapting energetically more favourable mushroom-conformations \[56,57\]. In another work, P12MA of similarly low grafting density (0.065 nm\(^{-2}\)) was grafted from a mica surface and showed a swelling ratio of 12 in hexadecane \[19\], in line with nSCF theory of increased swelling with decreasing grafting density \[58\].

Despite the large indentation depth with respect to the swollen thickness and the presumably non-homogeneous (gradient) structure in a swollen state, the force-indentation curves were fitted using Hertzian contact mechanics, even beyond the usual limit of 10% of strain. This would hold for the HD and MD regions, where the polymer chains were very likely in a stretched brush conformation. For the LD region and the assumed mushroom conformation, on the other hand, the elastic and the osmotic contributions could both be increasing with increasing indentation. This, in turn, could result in comparable evolution of the contact moduli for all three grafting densities, but it would be erroneous to assume a similar conformation for all three samples based on the evolution of the moduli alone. Nevertheless, when considering the confinement effects of the liquid permeating through variously dense brushes with different conformations, the differences between the samples become far more apparent.

Inspecting Fig. 4, it is clear that indentations taking place at increasing rates reach higher forces at a specific indentation depth—an effect attributed to both fluid-confinement as well as viscoelastic response of solvated polymer brushes. This behaviour is in line with the response observed upon rate-dependent indentation on macroscopic hydrogel samples using the same indentation methodology \[36\]. While for HD-P12MA the response upon indentation and corresponding relaxation during the dwell phase is strong, its magnitude reduces upon decreasing grafting density in the MD- and LD-P12MA brushes.

In order to quantify and compare the forces measured for the previously mentioned reasons.

The contact modulus during the first 10–20% of indentation showed very low values of about 0.3 kPa for all three grafting densities. Although the modulus values lie below previously published values reported for comparable polymer brushes \[19\], the values are reliable, due to the very accurately determined contact point. The analysis of the initial 10% of the indentation curve also avoids possible substrate effects during compression. The very low, but somewhat similar, value of the elastic modulus measured at the surface of all three samples most probably indicates that all three samples have some loose, dangling chains stretching out in the solvent, due to dispersity effects. However, given the relatively large error bars compared to the value at that point, it is difficult to claim that the values are exactly the same for all three samples.

Upon further indentation, the moduli increase significantly for all three grafting densities. Although the evolution of the contact moduli with indentation seems to be similar for all samples, especially when normalized to the total layer thickness (Fig. 6b), the measured moduli alone do not necessarily correspond to the same conformation of polymer chains. As described by Pasche et al., the polymer concentration during the indentation increases, as does the osmotic pressure. However, the elastic restoring force of a dense polymer brush can actually decrease during this process \[59\]. This would hold for the HD and MD regions, where the polymer chains were very likely in a stretched brush conformation. The very low, but somewhat similar, value of the elastic modulus measured at the surface of all three samples most probably indicates that all three samples have some loose, dangling chains stretching out in the solvent, due to dispersity effects. However, given the relatively large error bars compared to the value at that point, it is difficult to claim that the values are exactly the same for all three samples.

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In order to quantify and compare the forces measured for the
different indentation rates, the stiffening with respect to the force determined for the zero-rate indentation (0 μm/s) was calculated along the depth of indentation δ according to equation (6):

$$\text{Stiffening}(\delta) = \frac{F_x - F_0}{F_0}$$

where $F_x$ is the force measured at velocity $x$ and depth $\delta$, and $F_0$ is the force of the purely elastic response at the same indentation $\delta$.

Fig. 7 shows force stiffening upon indentation at various rates for the three grafting densities. At the slowest rate of indentation, very-little-to-no stiffening is observed for any of the grafting densities. Apparently, at this rate the fluid can be expelled from the region undergoing compression without any confinement effects occurring. The stiffening at the slowest rate for the MD brush, however, shows a peak at about 50 nm, which is unexpected, assuming a uniform stiffening throughout the layer thickness at this rate. While the function used for fitting describes the HD and LD very well, it underestimates the forces for the MD at indentation depths of 50 nm. Consequently, the stiffening
is slightly overestimated for the MD brush in this region. In the case of an ideal fit, the stiffening at the slowest indentation should be low and constant as seen for the HD and LD brushes. Increasing the rate of indentation clearly shows increased values of stiffening for all the P12MA layers, although the stiffening is more pronounced for increasing grafting densities. For HD-P12MA (Fig. 7a), the stiffening gradually decreases with increasing depth of indentation—indicative of possible confinement effects causing apparent stiffening throughout the layer thickness. The decay could be originating from the compression of the brush, as liquid is expelled from within, leading to a gradual decrease of the stiffening effect as less fluid is available. A sole contribution by osmotic pressure has recently been challenged in the work of Abbott et al. [58], i.e. both mechanical fluid confinement and related poroelastic phenomena could be jointly contributing to the observed mechanical behaviour. For decreased grafting densities, MD-P12MA and LD-P12MA, the stiffening is more pronounced within the top of the layer and sharply declines thereafter. The sharp decline, particularly visible for LD-P12MA, could be attributed to easier migration of the fluid through the lower-density polymer brush. Despite the large error bars, clear trends can be observed for the different grafting densities, nevertheless future work will aim at further improving the indentation method.

3.3. Confinement-dependent force relaxation

After reaching a force set-point at a given indentation rate, the piezo movement was stopped (dwell phase) and force relaxation followed, due to the vanishing of the poro- and viscoelastic effects. A dwell phase of 1 s was sufficient to achieve complete force relaxation. Such a decrease in force can be seen in the magnified force-distance plots in Fig. 4. However, plotting the force relaxation as a function of time in Fig. 8 enables much clearer comparison between the different grafting densities. For HD-P12MA during the dwell phase, a strong force relaxation can be observed upon increasing the rate of indentation, Fig. 8a. At 0.2 μm/s only minor relaxation is observed, indicative that the layer was drained of fluid already upon indentation. At increasing indentation rates however, the force relaxation over time clearly indicates an initial confinement effect. Such behaviour is characteristic of a poro- or viscoelastic material response, as reported for polymers [34] as well as hydrogels [25,60]. For decreasing grafting density, the force relaxation is less pronounced, presumably since the sparser structures are drained to a larger extent at comparable pressures. While this observation also supports the theory of fluid confinement through mechanical retention of the fluid within the porous brush structure, since all layers are considerably compressed, future experiments should aim at indentations of either thicker layers or at a lesser degree of compression.

4. Conclusions

In this study, polymer brushes of equal molecular weight, yet differing in grafting density, were compared in terms of structural and mechanical properties. The measured grafting densities in combination with the observed compression upon indentation revealed a densely packed brush-like layer for MD- and HD-P12MA, while despite a high swelling ratio, the sparsely spaced chains for LD-P12MA arrange in a more mushroom-like conformation. Theoretical calculations confirm that the observations are in line with the scaling [56] and crowding theories [57].

Upon accurate determination of the point of contact, comparison of the modulus development upon indentation yielded a comparable elastic modulus for the differently dense P12MA brushes of about 0.3 kPa. This is the first report of grafting-density-independent modulus determination using a conventional CP-AFM setup, extending the insight gained from earlier complex eSFA experiments [19]. Apparently, the methodology employed allows for accurate determination of the mechanical properties of ultra-thin ultra-low-moduli materials—a capability that is of great potential utility in several disciplines such as tissue engineering and bio-inspired coatings.

Calculation of a theoretical zero-rate indentation allowed an in-depth study of the fluid-confinement and viscoelasticity-related stiffening. The stiffening behaviour analysis revealed a clear dependence
on the grafting density indicative of confinement- and viscoelasticity-related effects supporting the load applied upon increased indentation rate. Following the indentation, relaxation of the probe showed a clear indication of a fluid outflow from within the contact area, which was most pronounced for HD-P12MA.

The indentation analysis of varying-grafting-density P12MA yielded new insights into the challenges of contact-point determination for soft, thin, viscoelastic polymers in the presence of a good viscous solvent. The methodology highlighted the force offset upon non-zero rates of indentation and provides a means to account for it. Analysis of the mechanical properties revealed the actual low modulus, previously overestimated by orders of magnitude due to viscous effects upon contact between the colloidal probe and polymer brush as well as potential substrate effects. Ultimately the insight gained could help develop new soft materials, such as contact lenses or coatings for medical devices, whose properties are dependent on optimal moduli, fluid-confinement and viscoelastic effects.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2019.02.040.

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