

# Influence of Confinement on the Chain Conformation of Cyclic Poly(*N*-isopropylacrylamide)

David Magerl,<sup>†</sup> Martine Philipp,<sup>†</sup> Ezzeldin Metwalli,<sup>†</sup> Philipp Gutfreund,<sup>‡</sup> Xing-Ping Qiu,<sup>§</sup> Françoise M. Winnik,<sup>§,#</sup> and Peter Müller-Buschbaum<sup>\*,†</sup>

<sup>†</sup>Lehrstuhl für Funktionelle Materialien, Physik-Department, Technische Universität München, James-Frank-Str. 1, 85748 Garching, Germany

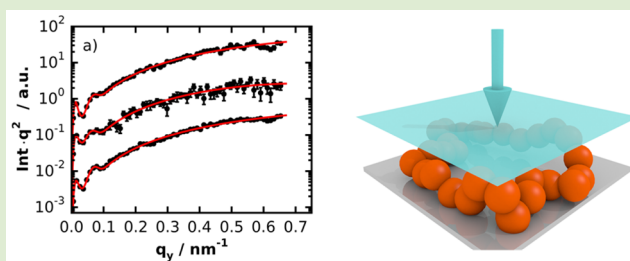
<sup>‡</sup>Institut Laue-Langevin, 71 avenue des Martyrs, 38000 Grenoble, France

<sup>§</sup>Faculty of Pharmacy and Department of Chemistry, Université de Montréal, CP 6128 Succursale Centre Ville, Montréal QC H3C 3J7, Canada

<sup>#</sup>World Premier International (WPI) Research Center Initiative, International Center for Materials Nanoarchitectonics (MANA) and National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Japan

## Supporting Information

**ABSTRACT:** In thin and ultrathin supported films, the conformations of flexible linear polymer chains might be considerably confined, in particular, for film thicknesses smaller than a few times the radius of gyration. For ring polymers in solution or in melt, the radii of gyration are significantly reduced as compared to those of their linear counterparts. We study here the influence of geometrical confinement on the chain conformation of cyclic PNIPAM in silicon-supported films. Measurements are performed by grazing incidence small angle neutron scattering (GISANS). For all films, the component of the radius of gyration parallel to the substrate,  $R_{g\parallel}$ , is significantly higher than the unperturbed  $R_{g\parallel}$  determined under theta solvent or melt conditions. We attribute this effect to a preferential selection of stretched PNIPAM ring conformations in thin films and a preferential orientation of macromolecules parallel to the film interfaces with the substrate and air.



The chain conformation of flexible polymers near surfaces and in thin to ultrathin films is a fundamental problem in polymer physics. Recent experimental studies and computer simulations on linear polymers provide an, at first sight, partially controversial picture about confinement in thin to ultrathin films (i.e., with thicknesses of a few to one radii of gyration). Some groups observe almost unperturbed chain conformations, as compared to the bulk state, with only a slight trend toward chain expansion along the substrate.<sup>1–3</sup> Others observe significantly modified chain conformations in thin to ultrathin films.<sup>4–7</sup> According to these studies, on average, the chain segments of the polymers, which are in the vicinity of a substrate, seem to be oriented more parallel to the surface and therefore flattened along the surface normal. Thus, a distortion may be imposed on spherical Gaussian coils of linear polymers, which are adsorbed on surfaces or confined in thin to ultrathin films. Potential reasons for perturbed chain conformations are related to the geometrical confinement imposed by the interfaces and to molecular interactions with them. Systematic studies of thin to ultrathin polystyrene films suggest that this effect gets most pronounced as the thickness decreases toward the undisturbed, average radius of gyration. An increase by 50%

or more was reported for the component parallel to the substrate of the radius of gyration within ultrathin films.<sup>6,8</sup>

The behavior of ring polymers in solutions and in melts significantly differs from that of their linear counterparts for the simple reason that they do not possess chain ends. Ring polymers are known to adopt much more compact structures than linear macromolecules. The chain dynamics also significantly depend on the chain topology: for instance, the reptation motion is not expected to exist for cyclic polymer melts, in contrast to linear ones.<sup>9</sup> Structures, dynamics, and properties of ring polymers have been investigated experimentally and theoretically for solutions and melts.<sup>10–13</sup> However, so far, their behavior at interfaces has not been addressed in detail.

In the present study, we investigate the molecular confinement effects existing in thin to ultrathin silicon-supported films of unknotted polymer rings of low molar mass. Grazing incidence small angle neutron scattering (GISANS) enables us to study the shape adopted by the macromolecular coils within

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the films. As demonstrated earlier,<sup>8</sup> GISANS is an elegant technique to probe the component parallel to the interface of the ensemble-averaged radius of gyration,  $R_{g\parallel}$ , of the macromolecules (see [Supporting Information](#)). The chosen homopolymer is the classical thermoresponsive polymer poly(*N*-isopropylacrylamide).<sup>13–20</sup> However, the focus here is not on its phase transition behavior in aqueous environment,<sup>21–27</sup> but on the shape of the coils adopted within silicon-supported thin to ultrathin films. Cyclic PNIPAM, with a molar mass of about 12 kg/mol, has been used (details can be found in the [Supporting Information](#)). Three blend films of protonated and deuterated cyclic PNIPAM with thicknesses of 3.3, 9.8, and 117 nm have been spin-coated (thicknesses determined by X-ray reflectivity). The film thicknesses were chosen such as to correspond to about one, a few, and a multiple of the unperturbed radius of gyration of the macromolecular rings.

Due to differences in chain conformation adopted by linear and cyclic polymers, smaller ensemble-averaged radii of gyration are expected for cyclic chains as compared to their linear counterparts.<sup>28–31</sup> The mean square radius of gyration of cyclic polymers can be calculated by the Gaussian approximation as<sup>32</sup>

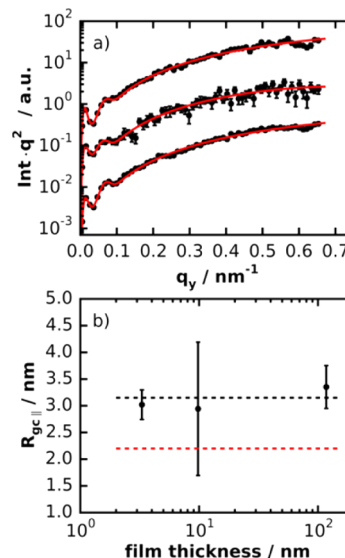
$$\langle R_{gc}^2 \rangle = \frac{nb^2}{12}$$

where  $n$  is the number of segments and  $b$  is the length of each segment (Kuhn length). In this framework, the ratio of the mean-square radii of gyration of cyclic and linear chains, the  $g$ -factor  $\langle R_{gc}^2 \rangle / \langle R_{gl}^2 \rangle$ , was calculated to be of 0.5 in theta solvents.<sup>32</sup> Experimental agreement with a  $g$ -factor of 0.5 over a wide range of molecular weights was reported.<sup>9,33,34</sup> In the following, we denote as  $R_g$  the square root of the mean square radius of gyration of the whole distribution of radii,  $R_g = (\langle R_g^2 \rangle)^{1/2}$ . The PNIPAM rings investigated are of rather low degree of polymerization (around 100) compared to those of most studies on cyclic polymers in solutions and in melts. The above-mentioned literature is nevertheless suitable to gain an estimate for the lower limit of the unperturbed radius of gyration of the cyclic PNIPAM under theta solvent or melt conditions. It equals to about 1.5 nm for the studied cyclic PNIPAM. The calculation is based on a Kuhn length  $l_k$  of 1 nm for PNIPAM, derived from a persistence length  $l_p$  of 0.5 nm.<sup>35</sup> Slightly different Kuhn lengths (e.g.,  $l_p = 0.7$  nm<sup>36</sup>), anyhow, have only a minor influence on the estimated  $R_{gc}$ .

The radius of gyration of low molar mass PNIPAM homopolymers has so far only been determined for the linear topology, but not for cyclic PNIPAM, under theta solvent conditions.<sup>37,38</sup> For a linear PNIPAM of 92 kg/mol,  $R_{gl}$  corresponds to  $6.0 \pm 0.3$  nm.<sup>37</sup> Using temperature-dependent small angle X-ray scattering (SAXS), we determined the unperturbed  $R_{gc}$  for a dilute aqueous solution of the cyclic PNIPAM near theta solvent conditions (see [Supporting Information](#)). The unperturbed  $R_{gc}$  of the PNIPAM rings lies around 2.2 nm. They are thus in agreement with the above theoretical estimation. Moreover, they are consistent with the  $R_{gc} = 2.2$  nm, determined for a 12 kg/mol cyclic polystyrene (having an identical backbone and a similar monomer molar mass than PNIPAM).<sup>39</sup> Thus, the Gaussian approximation might underestimate by at most 50% the real  $R_{gc}$  value for the theta solvent condition. Because of intrinsic chain stiffness, the real ensemble-averaged radius of gyration of the low molar

mass rings is probably higher than estimated by the Gaussian approximation.

Quantitative evaluation of the GISANS data sets acquired for the three cyclic PNIPAM films is done by line cuts through the 2D scattering data as described in the [Supporting Information](#). The related line cuts are shown in [Figure 1a](#) in the Kratky



**Figure 1.** (a) Kratky plot of the horizontal line cuts of the 2D GISANS data. Black dots are data; red lines correspond to the fits described in the text. Curves are shifted vertically for clarity. The film thickness increases from bottom to top: 3.3, 9.8, and 117 nm. Due to a lower acquisition time of the GISANS data of the 9.8 nm film, the statistics of the related line cut is reduced. (b) In-plane component of the radius of gyration  $R_{g\parallel}$  vs film thickness. The black, dashed line is a guide to the eye at 3.15 nm. The undisturbed radius of gyration obtained by SAXS (see [Supporting Information](#)) is 2.2 nm, indicated by the red, dashed line.

representation. All three curves have a quite similar shape. The two peak-like structures below  $q_y = 0.1$  nm<sup>-1</sup> of the three line cuts are related to the instrumental resolution and a feature that originates from the silicon substrate. The information about the in-plane component of the radius of gyration  $R_{g\parallel}$  of the cyclic PNIPAM chains is gained from the region between  $q_y = 0.1$  and  $q_y = 0.65$  nm<sup>-1</sup>.

In line with earlier publications,<sup>8</sup> the in-plane component of the radius of gyration  $R_{g\parallel}$  is extracted from the line cuts of [Figure 1a](#) using the Born approximation. In the case of linear polymers, the scattering function, or the form factor of a Gaussian coil, depends on the radius of gyration  $R_{gl}$ , according to the classical Debye function:<sup>29,31</sup>

$$P_l(q) = \frac{2}{q^4 R_{gl}^4} (e^{-q^2 R_{gl}^2} + q^2 R_{gl}^2 - 1) \quad (1)$$

Using the Gaussian approximation, the form factor of a cyclic chain under polymer melt conditions is given by<sup>29,31,40</sup>

$$P_c(q) = 2 \int_0^1 dx (1-x) \cdot \exp[-2q^2 R_{gc}^2 x(1-x)] \quad (2)$$

where  $R_{gc}$  denotes the radius of gyration of the cyclic chain. The curves of [Figure 1a](#) are fitted with a model using a Padé approximant based on eq 2.<sup>31</sup> It has to be noted that only the ensemble averaged value of the  $R_{gc}$  is obtained this way, but not

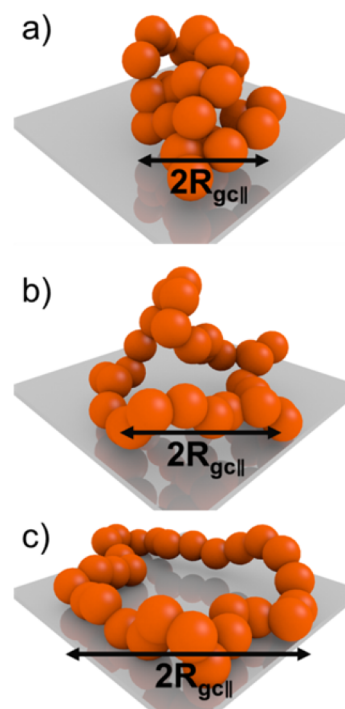
the whole distribution of  $R_{gc}$ . This means, in particular, that no information about structural changes along the film depth or about the width of the distribution of radii of gyration can be retrieved from the fits. To fit the full curves, the contributions from the instrumental resolution (a stretched Lorentzian function), the peak from the silicon substrate (a Gaussian function), and a symmetric, quadratic background are considered. Due to the low scattering intensity resulting from the small polymer rings, the evaluation of the background needs to be done very carefully: It is determined at high  $q_z$  values in the respective 2D GISANS patterns, where no scattering induced by the thin PNIPAM film occurs and thus the background is accessed directly.

Figure 1b depicts the fitted component parallel to the interface of the radius of gyration  $R_{gc||}$  versus the film thickness. Note that  $R_{gc||}$  of the PNIPAM rings in the films has an absolute value of about  $3.0 \pm 0.5$  nm and does not depend on film thickness, within error bars. These findings are remarkable for the following two reasons. First, even for the thickest film,  $R_{gc||}$  lies above the unperturbed radius of gyration  $R_{gc} = 2.2$  nm (determined by SAXS for theta solvent conditions, see Supporting Information). Second,  $R_{gc||}$  actually remains constant independent of film thickness within the margin of error, instead of decreasing with thickness. To our knowledge, the combination of these two effects has not been observed before for linear homopolymer chains in thin to ultrathin supported films. In cases where no thickness dependence was observed,  $R_{g||}$  was reported to correspond to the unperturbed  $R_g$  value for linear homopolymers.<sup>1–3</sup> In contrast, if a thickness dependence was noticed, increased  $R_{g||}$  values were found.<sup>4–8</sup> It seems that for cyclic polymers, confinement or trans-interfacial interactions in thin films lead to effects related to chain stretching and orientation, which are different from those observed for linear polymers.

We discuss first the possible confinement effects in case of the thinnest film having an average film thickness of 3.3 nm. Simple geometrical considerations show that the component perpendicular to the interface of the radius of gyration,  $R_{gc\perp}$ , has to be less than half the film thickness for this film. Hence, we surmise  $R_{gc\perp} = 1.6$  nm at maximum. Assuming that the stiffness of the small rings hinders their significant compression, the aspect ratio of the parallel and the perpendicular component of the radius of gyration equals to 2:1 or even more for the thinnest film. For sure, the ring polymers cannot adopt the shape of an isotropic coil within this thinnest film. They need to be rather “flat” and in addition oriented preferentially parallel with respect to the film/substrate interface.

Molecular dynamic simulations help to understand the structure adopted by such highly anisotropic coils of cyclic polymers. Figure 2 shows sketches of three different conformations out of the full distribution of the unperturbed  $R_{gc}$  of polymer melts with similar molar mass.<sup>41</sup> In the melt state, the coil-like conformation shown in Figure 2b is of higher probability than the compact conformation depicted in Figure 2a, or the stretched conformation of Figure 2c. We conclude from our findings that out of this whole distribution of  $R_{gc}$ , the stretched one seems to be highly preferred in case of the ultrathin film. Indeed, within the strongly limited height of such ultrathin films, this conformation might be favorable for the low molar mass rings.

In the 9.8 nm thick and 117 nm-thick films all degrees of chain stretching and chain orientation might in principle be geometrically allowed, while in the thinnest film only a



**Figure 2.** Sketches of three different conformations out of the full distribution of the unperturbed  $R_{gc}$ , inspired by molecular dynamics simulations.<sup>41</sup> Depicted are (a) a compact conformation from the lower end of the distribution, (b) a coiled conformation around the mean  $R_{gc}$ , and (c) a wide conformation oriented parallel to the surface.  $R_{gc||}$  increases from (a) to (c).

stretched conformation with an orientation parallel to the surface can occur. Of course, interfaces are also present for the thin and thick films. Extrapolating from the behavior of linear flexible polymers of much higher molar mass, one may assume that the interfaces impose significant restrictions to the polymer rings in the 5  $R_{gc}$  film. For the 55  $R_{gc}$  film, one could assume that its central part could have an unperturbed chain conformation. However, also for the thin and thick films,  $R_{gc||}$  significantly exceeds the value of the unperturbed radius of gyration. We exclude a nonequilibrium conformation due to spin-coating as the origin of the increased  $R_{gc||}$  since it would lead to a reduced value, as detailed in the Supporting Information. Therefore, we conclude that another long-range effect dominates the behavior of the low molar mass rings studied here than for larger linear chains. In planar film geometry, van der Waals forces are known to form long-range interactions between polymer chains and substrates.<sup>42,43</sup> We surmise that they may facilitate the preferential selection of the stretched conformation of the PNIPAM rings, as well as induce the same orientation effect of the rings parallel to the substrate for all film thicknesses. Thus, the 55  $R_{gc}$  film might still be dominated by its interfaces, and a transition to bulk-like films does not occur until much larger thicknesses are reached.

Different molecular confinement mechanisms probably codetermine the conformation of ring polymers, as compared to linear macromolecules, in thin to ultrathin films, since ring polymers do not possess any chain ends and generally adopt more compact structures than their linear counterparts. Such potential strong confinement effects are investigated for low molar mass cyclic PNIPAM chains in thick to ultrathin films. Three films of a blend of protonated and deuterated cyclic PNIPAM, with thicknesses of 3.3, 9.8, and 117 nm are



prepared. The unperturbed, ensemble-averaged radius of gyration  $R_{gc}$  amounts to 2.2 nm under theta solvent, or melt conditions. Remarkably, our GISANS measurements reveal larger absolute values of the component parallel to the substrate of the radius of gyration  $R_{gc\parallel}$  of  $3.0 \pm 0.5$  nm in the films. Moreover, this large  $R_{gc\parallel}$  value is independent of film thickness. We conclude that out of the whole distribution of  $R_{gc}$  existing in the melt, the one corresponding to the stretched conformation is highly preferred in the case of the films. Furthermore, on average the chains adopt an orientation parallel to the substrate. For the ultrathin film, these effects might be imposed by geometrical constraints. However, this cannot hold true for the 55  $R_{gc}$  film. We surmise that long-range van der Waals forces might contribute to the average stretched chain conformation for the considered film thicknesses.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00676.

Experimental details to sample preparation, GISANS, and SAXS measurements (PDF).

## ■ AUTHOR INFORMATION

### Corresponding Author

\* E-mail: muellerb@ph.tum.de.

### Notes

The authors declare no competing financial interest.

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