### **Supporting Information**

# Self-similar Polymer Ring Conformations base on Elementary Loops – a direct Observation by SANS

### Margarita Kruteva<sup>1\*</sup>, Jürgen Allgaier<sup>1</sup>, Michael Monkenbusch<sup>1</sup>, Lionel Porcar<sup>2</sup>, Dieter Richter<sup>1</sup>

<sup>1</sup> Jülich Centre for Neutron Science (JCNS) & Institute for Complex Systems (ICS), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

<sup>2</sup> Institut Laue-Langevin (ILL), B.P. 156, F-38042 Grenoble cedex 9, France

### 1. Ring synthesis and characterization

#### Synthesis

The procedure for the synthesis of the PEO rings up to 20 kg/mol (R10 and R20) is described in reference 1. In this process the ring formation of HO-PEO-OH is carried out with the help of p-toluenesulfonyl chloride (TosCl) in the presence of KOH. The intermediately formed tosylation product HO-PEO-OTos reacts with still unreacted OH-end groups under the formation of an ether bond. In a dilute solution and considering that the ring closure reaction is much faster than the tosylation reaction, predominantly unimeric rings are formed by reaction of a tosylated chain end with the still OH-functionalized second end of a chain. As the samples were synthesized in gram quantities, the ring closure reactions were carried out at moderate dilution conditions which lead to visible amounts of chain coupling, but the main product was the unimeric ring.

For the synthesis of rings with higher molecular weights than 20 kg/mol (R40 and R100) this procedure was not useful and led to very low ring yields. The main reason for these limitations is the decreasing concentration of reactive groups with increasing molecular weight, which drastically slows down the reactivity in the tosylation step, where OH-PEO-OH reacts with the activation agent TosCl. Therefore, for the synthesis of the R40 and R100 rings a different strategy was chosen. In the new process the linear PEO precursors were synthesized using the potassium salt of di(ethylene glycol) monobenzyl ether (BnO-(EO)2-OK) as initiator for the polymerization of ethylene oxide, yielding mono-alcoholic BnO-PEO-OH. This compound was immediately tosylated with a large excess of TosCl to BnO-PEO-Tos, followed by the cleavage of the initial benzyl group with H2/PdC which

<sup>\*</sup> Corresponding author: m.kruteva@fz-juelich.de

leads to HO-PEO-OTos. This compound was used for the ring closure reactions. The amount of unimeric rings in the cyclization raw products ranged from 30 to 50%, depending on the molecular weight. Unreacted linear precursor and chain coupled higher molecular weight linear byproducts were eliminated from the cyclization raw products by oxidizing the alcoholic chain ends to carboxylic acids and removing the oxidized material with the help of a basic ion exchange resin. Because of the very low concentrations of carboxylic acid head groups in the case of the R40 and R100 polymers, a very fine-grained ion exchange resin (SourceTM 15Q) had to be used in order to efficiently remove the oxidized linear material. Smaller quantities of higher molecular weight cyclic PEO were finally removed by fractionation using chloroform/heptane as solvent/non-solvent pair. Deuterated rings were prepared in the same way as the hydrogenous counterparts and contained as a consequence of the used initiator two hydrogenous EO-units in the ring.

#### Characterization

SEC traces of the newly synthesized rings hR40, dR40, hR100, and dR100 are shown in Figure S1. For all chromatograms there is no higher molecular weight linear or ring shaped polymer visible at lower elution times. The same holds for the linear mother compounds having the same molecular weights as the ring polymers. For all chromatograms, the left flank of the product signal shows no indication of the linear polymer, whose elution time is about 0.5 min. lower than the one of the ring product. In order to test the sensitivity of the SEC method for the detection of linear byproduct, a sample of dR100 was contaminated with 1% of linear polymer. The SEC traces of dR100 and the contaminated sample are shown in Figure S2. The small shoulder between 18.75 min and 19.25 min shows the linear contamination, which is not present in the noncontaminated sample (see Fig.S2, insert) – there the baseline is flat. Therefore, we safely conclude that the fraction of linear chains in the hR40, dR40, hR100, and dR100 ring samples is below 1%. The R10 and R20 samples synthesized earlier contain higher fractions of linear polymer because the purification process of the raw products was less efficient (see main text and Ref. 1)<sup>1</sup>. It should also be pointed out that the quantification of linear chains by NMR end group detection (see ref. 1) did not work for the R40 and R100 rings because of the extremely small end group concentrations.



**Figure S1**: SEC chromatograms of the rings hR40, dR40, hR100, and dR100. The different elution time of hR40 and dR40 rely on different SEC setups.



**Figure S2**: SEC chromatograms of the ring dR100 with and without 1% of linear dL100. The insert magnifies the region between 18.7 and 19.4 minutes elution time.

## 2. Error calculation and correction for linear contaminant for the radii of gyration

**Error calculation:** As explained in the manuscript the errors of  $R_g$  were evaluated in calculating  $R_g$  at the one sigma statistical deviation of the fit parameters l and v that determine  $R_g$ . Table S1 presents the details:

**Table S1:** Radii of gyration calculated at the one sigma statistical deviation of the fractal exponent  $v = 1/d_f$  and the monomer length *l* 

Ring	Rg	1	$R_g(l + \Delta l)$	$R_g(l-\Delta l)$	ν	$R_{g}(\nu + \Delta \nu)$	$R_g(\nu - \Delta \nu)$
	[nm]	[nm]	[nm]	[nm]		[ <i>nm</i> ]	<i>[nm]</i>
R100	4.94	0.583 <u>+</u> 0.012	5.04	4.84	0.433 <u>+</u> 0.003	50.25	48.5
R40	3.56	0.561 <u>+</u> 0.012	3.63	3.48	0.448 <u>+</u> 0.003	36.0	35.0
R20	2.88	0.573 <u>+</u> 0.012	2.93	2.81	0.451±0.010	3.00	2.76
R10	2.17	0.555 <u>+</u> 0.012	2.21	2.11	0.460 <u>+</u> 0.003	2.18	2.14

The final errors were calculated from the sum of errors:

$$\Delta R_g = \sqrt{\frac{1}{2} \left[ \left( R_g(l) - \overline{R_g(l \pm \Delta l)} \right)^2 + \left( R_g(\nu) - \overline{R_g(\nu \pm \Delta \nu)} \right)^2 \right]}$$
E1

The results are found in Table 1 of the manuscript.

**Correction for linear contaminants**: Scattering observes the z-average of the radii of gyration. The narrow molecular weight distribution does not result in any important correction. The admixture of linear contaminants needs to be scrutinized. The z-average is calculated as

$$\langle R_g^2 \rangle_z = \frac{\sum w_i M_i \langle R_g^2 \rangle_i}{\sum w_i M_i}$$
 E2

where  $w_i$  are the mass fractions and  $M_i$  the component masses. Since the masses of the ring and the leading linear contaminant are equal, E2 reduces to

$$\langle R_g^2 \rangle_z = \frac{\sum w_i \langle R_g^2 \rangle_i}{\sum w_i}$$
E3

With the size of the linear component  $\langle R_g^2 \rangle_{lin} = \frac{1}{6} l^2 N$  we may equate E2 to:

$$\langle R_g^2 \rangle_{ring} = \frac{\langle R_g^2 \rangle_{observed} - w_{lin} \langle R_g^2 \rangle_{lin}}{w_{ring}}$$
 E4

With the linear weight fractions obtained from characterization, table S2 presents the corrections:

**Table S2**: Corrections for the radii of gyration as a consequence of linear contaminants

Ring	Wlin	Correction $\Delta R_g^{ring}$ [nm]
R100	> 1%	> -0.08
R40	> 1%	> -0.04
R20	3.5%	- 0.1
R10	1.5%	-0.03

For the two largest rings the correction will be smaller than the quoted values. The exact amount cannot be given since the linear contamination came out to be smaller than 1%. We estimate that half of the quoted value is the true value. In Table 1 of the main manuscript we have corrected for half of  $\Delta R_g^{ring}$  and added the other half to the uncertainty.

#### 3. Absence of Flory Huggins - Parameter

Fig. S3 displays SANS results from the R100 ring taken at different volume fractions of the deuterated component. The data were normalized to the deuterated volume fraction. As may be seen the data perfectly superimpose to each other. Thus, there is no notable Flory-Huggins parameter  $\chi$  between the hydrogenated and deuterated rings. As  $\chi$  is negligible for the largest rings, there will be no influence at smaller rings.



**Figure S3:** SANS data for R100 rings normalized to the concentration and sample volume (see the legend). The data for 0% indicate the SANS intensity extrapolated to zero concentration.

#### 4. The elementary loop size – ssq as a function of $N_{e,0}$

In order to investigate the statistical uncertainty of the elementary loop size, we calculated the residual sum of errors ssq for different fixed values of  $N_{e,0}$ . Fig. S4 displays ssq as a function of  $N_{e,0}$  that shows a well defined minimum at  $N_{e,0}$  = 45.



**Figure S4**: Residual sum of errors as a function of fixed values for  $N_{e,0}$ .

#### 5. The fractal dimension - comparison with atomistic simulation

As may be seen from Figure S5, the properly normalized simulation data taken from Ref. 2<sup>2</sup> indicate the mass fractal regime beyond  $N/N_{e,0}=n \approx 15$ . The blue vertical line displays the largest n=44 that we have reached. Our SANS data clearly show that at this n the mass fractal regime is not achieved. The ring fractal dimension at n=44 remains at  $d_f=1/v=2.33$ , far away from the mass fractal regime at  $d_f=3$ . We further note, that a compilation of simulation data by Halverson *et al.* <sup>3</sup> also indicated mass fractals beyond n=15.



**Figure S5:** Dependence of the ring  $\langle R_g^2 \rangle$  on the reduced chain length from Ref. 2 <sup>2</sup> For the references to the other simulation and experimental data see the original paper <sup>2</sup>. Vertical blue line shows the largest reached n value in our work.

## 6. Insensitivity of the fit on the sharpness of the transition from the Gaussian to the fractal regime.

In the main manuscript we have quoted that the fit quality of the SANS data is insensitive to the sharpness of the transition  $v_{width}$  between the Gaussian and fractal exponents describing the different conformational regimes of the ring polymer. Figure S6 displays fitting results to the SANS data choosing  $v_{width=1}$ , 3, 5. While the other fit parameters were not affected, the quality of data description does not change for different  $v_{width}$ .



(a)



(b)



**Figure S6**: SANS based form-factors observed for rings of different molecular weights covering the range  $5 \le N/N_{e,0} \le 44$ . For better visibility the data are shifted vertically by a factor of 2 with respect to each other. The solid lines are the results of joint fits with Eqs. 3 (see main text) fixing v<sub>width</sub> to 1 (a),3 (b),5 (c).

#### 7. The power law regime in $R_g(N)$

Even though we have studied only 4 different ring sizes, we still may ask, whether within the errors the slope connecting the two smaller rings is larger than that connecting the tow larger ones. Fig. S7 shows the result of this exercise. We note that indeed the two slopes differ slightly: between the 10K and 20K rings the slope appears to be  $v_{R_g} = 0.39$ , while for the two larger ones the slope reduces to  $v_{R_g} = 0.36$ . These differences may not be significant but show that with larger ring sizes the relative increase of  $R_g$  seems to diminish.



**Figure S7**: Ring radii of gyration  $R_g$  as a function of ring size  $N/N_{e,0}$ . Dashed dotted black line indicates the mass fractal power law  $R_g \sim \left(\frac{N}{N_{e,0}}\right)^{1/3}$ . Blue lines are fits with a power law.

#### References

- Hövelmann, C. H.; Gooßen, S.; Allgaier, J. Scale-Up Procedure for the Efficient Synthesis of Highly Pure Cyclic Poly(Ethylene Glycol). *Macromolecules* 2017, 50 (11), 4169–4179.
- (2) Tsalikis, D. G.; Alatas, P. V.; Peristeras, L. D.; Mavrantzas, V. G. Scaling Laws for the Conformation and Viscosity of Ring Polymers in the Crossover Region around *M*<sub>e</sub> from Detailed Molecular Dynamics Simulations. *ACS Macro Lett.* **2018**, *7* (8), 916– 920.
- Halverson, J. D.; Grest, G. S.; Grosberg, A. Y.; Kremer, K. Rheology of Ring Polymer Melts: From Linear Contaminants to Ring-Linear Blends. *Phys. Rev. Lett.* 2012, *108* (3), 038301.