Chain Conformation of Poly(alkylene oxide)s Studied by Small-Angle Neutron Scattering

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Supporting Information

ABSTRACT: Using small-angle neutron scattering, the unperturbed chain dimensions of a series of poly(alkylene oxide)s (PAO’s) were studied as a function of side-chain length. The PAO’s were obtained using anionic ring-opening polymerization methods. The deuterated monomers were synthesized from commercially available precomponents. A systematic decrease of the chain dimensions with increasing length of the side chains was found. We also compare the PAO’s with the chemically very similar poly(olefin)s with respect to the characteristic ratio $C_{\infty}$, the chain dimensions, and the packing length as a function of the molecular weight per backbone bond. In doing so, we found significant differences between the static properties of the two systems.

■ INTRODUCTION

Studying the unperturbed chain dimensions has long been and still is a major topic in polymer science, 1–8 and especially the homologous series of the poly(olefin)s has been studied extensively over the last decades. 9–14 The poly(olefin)s have side chains of varying length and exhibit a systematic decrease of the glass transition temperature $T_g$ with increasing length of the side chains. 13–15 This is a feature reported also for other side-chain polymers, e. g. the poly($n$-alkyl acrylate)s and poly($n$-alkyl methacrylate)s. 16–19 In contrast, the homologous series of the poly(alkylene oxide)s (PAO’s) shows a virtually constant glass transition temperature. 20 Therefore, a detailed study of the chain conformation of the PAO’s would be highly interesting. Up to now, the radius of gyration $R_g$ of poly(butylene oxide) has been determined only in theta-solvent a long time ago, 7 and in a recent study of poly(octylene oxide)—poly(ethylene oxide) diblock copolymers $R_g$ of poly(octylene oxide) is given. 21

Here we present the first ever systematic study of the unperturbed chain dimensions of a series of poly(alkylene oxide)s (PAO’s). We used small-angle neutron scattering (SANS) to study the chain conformation of the PAO melts by using a mixture of protonated and deuterated polymers, focusing thereby on the variation of the length of the side chains. Below, we report the synthesis and characterization of deuterated monomers for three different PAO’s. The resulting virtually monodisperse samples together with previously synthesized protonated polymers 22 now allowed for the first experimental exploration of the relation of the PAO-chain dimensions to molecular weight per backbone bond $M_N$: Various techniques were exploited to accurately determine the radius of gyration, and quantities like the packing length $p$ and the characteristic ratio $C_{\infty}$ are derived. The results are discussed in terms of the backbone equivalence model 17 and compared to the poly(olefin)s.

The paper is organized as follows. In the experimental section the polymer synthesis and sample composition is introduced, and the SANS method is presented. In the Theory section, a brief overview over the necessary scattering functions for the data modeling is given. Then in the Results and Discussion, the experimental results are presented and discussed.

■ EXPERIMENT

Polymer Synthesis and Analysis. Materials. 1-Bromobutane-$d_0$, 1-bromohexane-$d_{15}$, and 1-bromooctane-$d_{17}$ (all Isotec, 98 atom-% D), N,N-dicyclohexylmethylamine (Aldrich, 97%), 3-chloroperbenzoic
acid (Aldrich, 70.5% peracid), diethyleneglycol dibutyl ether (Aldrich, ≥99%), and diethyl ether (Aldrich, ≥99%) were used as received.

**General Synthetic Procedures.** The deuterated monomers were synthesized from commercially available fully deuterated 1-bromoalkanes. In the first reaction step the 1-bromoalkanes were converted into the corresponding 1-alkenes by elimination of HBr. The deuterated 1-alkene oxide monomers were obtained by oxidizing the 1-alkenes using 3-chloroperbenzoic acid. The progress of the oxidation reaction was controlled by determining the residual peroxide via titration of samples taken at different times with the potassium iodide - sodium thiosulfate system. For the synthesis of the hydrogens polymers commercially available 1-alkene oxide monomers were used. Before polymerization the monomers were dried over CaH₂ according to ref 22. The anionic ring-opening polymerizations of the alkene oxides were carried out using the potassium tert-butanolate (KOT-Bu) and 18-crown-6 (18C6) initiating system. The mass ratio of monomer to the solvent toluene ranged between 0.8 and 1.1 and a polymerization temperature between −10 and −15 °C. In the case of the two polyoctylene oxides (cf. Table 1), the molar ratio of 18-C-6 to KOT-Bu ranged between 0.8 and 0.9 and the polymerization time was between 4 and 6 days. For the other polymers the molar ratio of 18-C-6 to KOT-Bu ranged between 3.0 and 3.2 and the polymerization time was between 5 and 9 days. The details of the polymerization reactions are described in ref 22.

**Monomer and Polymer Characterization.** Gas chromatography—mass spectrometry: The low boiling alkene oxides were analyzed by GC-MS on an Agilent 6890-GC, coupled with a Finnigan MAT 95sq-MS. The samples were GC-separated on a SGE BPXS column (25 m × 0.22 mm × 0.25 μm) with adequate temperature programmes. The helium flow was 1 mL/min (electronic pressure control). The mass spectrometer was used in the electron ionization mode (70 eV, ion source temperature 260 °C). The observed mass range was 50–800 Da and the scan duration was 0.74 s. All fractions from the low temperature distillations were investigated by GC-MS in several dilution steps. All samples were injected considerably overloaded with respect to the main product in order to reveal traces of impurities originating, e.g., from side reactions or solvent impurities in full scan spectra. This is especially essential for highly reactive compounds, which interfere in the course of next reaction steps. A semiquantitative estimation was achieved in a more diluted case. Because of the lack of deuterated standards, neither external nor internal calibration was possible. The differences of the response factors under electron ionization mode are indeed negligible in contrast to the ESI ionization; but for the detection/integration of impurity peaks especially in the sub-%-range the main product has to be saturated and therefore a general overestimation of all minor products took place.

The NMR spectra were obtained on a Varian Inova 400 MHz. All samples were measured at 295 K in CDCl₃ with a 5 mmPFG AutoX DB Probe. Chemical shifts are given in δ ppm using the residual proton signal of the deuterated solvent as reference (δ₀H(D)CDCl₃ = 7.24 ppm; δ₀D(CDCl₃) = 77 ppm).

The SEC experiments were carried out using a PL-GPC 50 instrument. Three PolyPore (Polymer Laboratories) 5 μm columns (molecular weight operating range 200–2,000,000 g/mol) at 30 °C were used. For the signal detection a Viscotek Model TDA 300 detector with differential refractometer (RI) detector at 650 nm and a 90° laser light scattering (LS) detector at 670 nm was used at 30 °C. The solvent was THF at a flow rate of 1 mL/min, which was degassed with a Viscotec Model VE 7510 instrument. Molecular weights were calculated from the results of the LS and RI detectors using the Polymer Laboratories Cirrus GPC software. Molecular weight distributions were obtained using conventional polystyrene calibration.

**Table 1. Sample Details of the PAOs**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mw [g/mol]</th>
<th>Mn/Mw</th>
<th>Nmono</th>
<th>ρ [g/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>h-PBO</td>
<td>43,500</td>
<td>1.02</td>
<td>604</td>
<td>0.98–7.2×10⁻⁴T</td>
</tr>
<tr>
<td>d-PBO</td>
<td>39,800</td>
<td>1.04</td>
<td>497</td>
<td>1.09–7.2×10⁻⁴T</td>
</tr>
<tr>
<td>h-PHO</td>
<td>41,700</td>
<td>1.08</td>
<td>417</td>
<td>0.94–6.9×10⁻⁴T</td>
</tr>
<tr>
<td>d-PHO</td>
<td>36,800</td>
<td>1.03</td>
<td>329</td>
<td>1.05–6.9×10⁻⁴T</td>
</tr>
<tr>
<td>h-POO</td>
<td>9870</td>
<td>1.07</td>
<td>77</td>
<td>0.92–6.6×10⁻⁴T</td>
</tr>
<tr>
<td>d-POO</td>
<td>11,900</td>
<td>1.02</td>
<td>83</td>
<td>1.04–6.6×10⁻⁴T</td>
</tr>
</tbody>
</table>

[a] Average number of monomers per polymer chain. [b] T in °C.

For the signal detection a Viscotek Model TDA 300 detector with differential refractometer (RI) detector at 650 nm and a 90° laser light scattering (LS) detector at 670 nm was used at 30 °C. The solvent was THF at a flow rate of 1 mL/min, which was degassed with a Viscotec Model VE 7510 instrument. Molecular weights were calculated from the results of the LS and RI detectors using the Polymer Laboratories Cirrus GPC software. Molecular weight distributions were obtained using conventional polystyrene calibration.

1-Butene Oxide-d₈. First, 150.4 g of 1-bromobutane-d₈ (1.03 mol) was heated together with 301.2 g of N,N-dicyclohexylmethyamine (1.54 mol) for 27 h in a 1 L steel autoclave to 160 °C. Because of the formation of 1-butene the pressure increased to 14 bar. After the heating was finished the autoclave was connected to a vacuum line and the butene was cryodistilled under vacuum conditions into a pressure tested flask equipped with a Teflon stopcock. The crude product obtained was purified by another cryodistillation step. For this distillation the 1-butene was cooled to dry ice temperature and distilled at the vacuum line into another flask, which was kept at liquid nitrogen temperature. Thus, 28.1 g of 1-butene-d₈ (44%) was obtained. The purity of the product was not examined. Instead, it was assumed that it was similar to the product, which was obtained under identical reaction conditions using hydrogenous 1-bromobutane. In that case the product contained according to ¹H NMR 96% of 1-butene, 3% of 2-butenes, and 1% of hydrogens cyclohexene.

1-Butene Oxide-d₁₂. First, 118.1 g of 3-chloroperbenzoic acid containing 0.48 mol of peracid was dissolved in 280 g of diethylene glycol dibutyl ether. The mixture was cooled to dry ice temperature and was degassed at a vacuum line. Then 28.1 g of 1-butene-d₁₂ (0.44 mol) was distilled into the reaction flask. The mixture was first warmed up to 0 °C and within 3 days it was brought to room temperature, where it was left for another 4 days. The crude product was isolated by cryodistillation at a vacuum line, whereby the flask containing the reaction mixture was kept at room temperature and the crude product was collected in a flask cooled to liquid nitrogen temperature. After drying over Na₂SO₄ the crude product was purified by distillation using a 30 cm vacuum-jacketed column, packed with 3 × 3 mm wire mesh rings (Normag). Prior to the distillation the 5.7 g of toluene were added as a polymerization inert substance to the crude product in order to increase the yield in the distillation step. The fraction distilling between 62 and 62.5 °C was collected for the polymerization experiments.

The analysis by ¹H NMR showed the presence of <1% of toluene. In order to quantify the toluene content tetramethylethanol (δ = 0 ppm) was added as a reference. The known weights of sample and reference allowed quantifying all present proton compounds. In the ¹H NMR spectrum only the signals of 1-butene could be detected. The GC–MS analysis revealed besides the main product 1-butenoxid-d₈ some toluene. Moreover, a very small peak at 14.7 min (0.2%) showed the presence of some 2-butenoxid-d₈.

1-Hexene-d₁₂. First, 200.4 g of 1-hexahexane-d₁₂ (1.12 mol) was heated together with 326.5 g of N,N-dicyclohexylamine (1.67 mol) for 7 h to 170–175 °C in a flask equipped with a reflux condenser. After the heating was finished the flask containing the reaction mixture was connected to a vacuum line and the hexene was cryodistilled under vacuum conditions into another flask. The crude product was purified by distillation using a 30 cm vacuum-jacketed column, packed with 3 × 3 mm wire mesh rings (Normag). The fraction distilling between 61.5 and 65.5 °C was collected for the oxidation. Thus, 41.7 g of 1-hexene-d₁₂ (43%) was obtained.

Analysis by ¹H NMR showed the presence of 1% of hydrogens cyclohexene. In the ¹3C NMR spectrum only the signals of 1-hexene could be detected. Signals of 2- and 3-hexenes were not visible. These results were confirmed by the ¹⁵N NMR spectra.
The analysis by $^1$H NMR showed the presence of $o$-xylene, cyclohexene oxide, ethanol, ethyl acetate, and ethyl formate. The quantitative analysis of the $^1$H NMR spectrum showed that all these compounds were found in amounts smaller than 0.5%. After the drying step over CaH$_2$ the product was analyzed by GC-MS. This investigation confirmed the presence of some $o$-xylene and cyclohexene oxide. The other impurities found in the NMR analysis, ethanol, ethyl acetate, and ethyl formate, were eliminated. However, additionally some chlorobenzene was detected. This compound was not found in the NMR analysis because of the uncertain sealing of the sample cells higher temperatures could have led to a possible degradation of the polymers, rendering the whole experiment useless.) Three different setups with sample-to-detector distances of $L = 1, 2, \text{ and } 8$ m, a collimation length of 8 m, and wavelength $\lambda = 7$ Å were used. The wavelength spread was $\Delta \lambda/\lambda \approx 10\%$. With these setups, the scattering vector $Q$ ranges from $7 \times 10^{-3}$ to $0.25$ Å$^{-1}$. The beam aperture was $10 \times 10$ mm$^2$. The raw data were corrected for scattering from the empty cell, detector sensitivity, and background noise. For measuring the latter, boron carbide is used to block the beam. Calibration in absolute units (cm$^{-1}$) is done by using a PMMA secondary standard:

$$
\left(\frac{d\Sigma}{d\Omega}\right)_s = \left(\frac{I_{pol}}{I_{bc}}\right)^2 T_x T_\text{inc} T_\text{det} \frac{\Delta \lambda}{\Delta \lambda_{pol}} \left(\frac{I_{pol}}{I_{bc}} - T_x (I_{bc} - I_{pol})\right)
$$

Here $I_{pol}$, $I_{bc}$, and $bc$ refer to the PMMA standard, sample, empty cell, and boron carbide, respectively. $T_x$ denotes the respective transmission, $I(Q)$ the scattered intensity, $b$ the sample thickness, and $L$ the sample-to-detector distance. $Q_{pol} = \left(\frac{I_{pol} - I_{bc}}{I_{bc}} - T_{pol}(I_{bc} - I_{pol})\right)$ is the averaged measured intensity of the PMMA, with the intensity of the empty beam $I_{bc}$. All transmissions are measured with a monitor inside the beam-stop at $Q = 0$.

After radial averaging the incoherent contributions of both protonated and deuterated chains were subtracted in order to obtain the absolute macroscopic differential cross sections $(d\Sigma/d\Omega)_{coh}(Q)$, hereafter abbreviated as $I_{pol}(Q)$. The correction for the incoherent background was realized by subtracting a constant $I_{inc,0}$ assuming a power law description for the data at high $Q$. The subtracted constants agreed well with the calculated incoherent scattering of the samples.

### THEORY

The scattering function of an ideal Gaussian chain in the discrete representation in the limit of infinite dilution is given by (e.g., in ref 24)

$$
I_{pol}(Q) = V \phi_{pol}(\Delta \rho)^2 S_{pol}(Q)
$$

$$
= V \phi_{pol}(\Delta \rho)^2 \frac{1}{N_{\text{mono}}} \left\{ N_{\text{mono}} 1 + b - 2b 1 - b N_{\text{mono}} \right\} (1 - b)^2
$$

where $V$ is the volume of a polymer chain, $\phi_{pol}$ the polymer volume fraction, $\Delta \rho = \rho_1 - \rho_2$ the scattering contrast with $\rho_1 (i = 1, 2)$ the corresponding scattering length densities (=SLD) of polymer and matrix or $\Theta$-solvent. $S_{pol}(Q)$ is the single chain structure factor, $N_{\text{mono}}$ is the number of monomers and $b = \exp (-Q^2/6)$ with the statistical segment length $l$. $Q = (4\pi/\lambda) \sin (\theta/2)$ denotes the momentum transfer, where $\theta$ is the scattering angle.
For large \( N_{\text{mono}} \) (i.e., \( \approx 100 \)), \( S_{\text{pol}}(Q) \) can be simplified to the Debye formula
\[
S_{\text{Debye}}(Q) = \frac{2}{x^2}(x - 1 + \exp(-x))
\]
with \( x = Q^2R_g^2 \), where the radius of gyration is given by
\[
R_g^2 = \frac{\int r^2\rho(\mathbf{r})\,d^3r}{\int \rho(\mathbf{r})\,d^3r} = \frac{1}{6}C_{\infty}n(l_0^3)
\]
with distance from the center of mass \( \rho \), SLD \( \rho_s \) characteristic ratio \( C_{\infty} \), and backbone bond number \( n = N_{\text{mono}} - n_0 \). There \( N_{\text{mono}} \) is the number of monomers per chain and \( n_0 \) the number of backbone bonds per monomer. \( \langle l_0^3 \rangle \) is the mean square of the different bond lengths \( l_0 \) in the backbone of one monomer (\( \langle l_0^3 \rangle^{1/2} \approx 1.54 \) Å for C–C single bonds, and \( \approx 1.43 \) Å for C–O single bonds\(^{25}\)).

Often, in a polymer isotope blend the protonated (‘\( h \)’) and deuterated (‘\( d \)’) species do not have the same degrees of polymerization: \( N_h \neq N_d \). A standard approach to account for this and for the isotope interaction is by a random phase approximation:\(^\text{24}\)
\[
\frac{\Delta \rho^2}{I_p(Q)} = \frac{1}{\phi_hV_0N_hS_h(Q)} + \frac{1}{\phi_dV_0N_dS_d(Q)} - 2\chi/V_0
\]
where \( \phi \) and \( N \) are the corresponding volume fraction and degree of polymerization of the two isotopes, \( V_0 \) is the average monomer volume, and \( \chi \) the Flory–Huggins interaction parameter.

An independent way for obtaining \( R_g \) and \( \chi \) is by a so-called Zimm analysis, i.e., plotting
\[
\frac{\phi(1-\phi)}{N_{\lambda}(\Delta \rho)^2 I_p(Q)} \text{ vs } Q^2 - k\phi(1-\phi)
\]
for small \( Q \) (i.e., \( QR_g \leq 1 \)) and several concentrations \( \phi \) yields \( \chi \) (mol/cm\(^2\)) = \( -(m_0)/(2k) \) with a constant \( k \) and \( m_0 \) being the slope of the extrapolation \( Q \rightarrow 0 \), and \( M_{\lambda} = (N_{\lambda})/\langle (\Delta \rho)^2 \rangle \gamma_0 \) with the extrapolation’s y-axis intercept \( \gamma_0 \). Extrapolating \( \phi \) = 0 gives the radius of gyration \( R_g = (3V_{\text{chain}}m_\phi)^{1/2} \) with the extrapolation’s slope \( m_\phi \).

## RESULTS AND DISCUSSION

Hydrogenous polyalkylene oxides having narrow molecular weight distributions up to high molecular weights can be synthesized by anionic ring-opening polymerization.\(^{1} \) In contrast to the hydrogenous monomers, the deuterated analogues are not commercially available. They were synthesized using commercially available perdeuterated 1-bromoalkanes as starting materials. By eliminating HBr the corresponding 1-alkenes were obtained. It is compulsory to carry out this reaction with the help of a bulky base such as tertiary amines in order to suppress the subsequent isomerization by migration of the double bond. Besides the isomerization products of the 1-alkenes cyclohexene was found in the product mixtures. This compound is a decomposition product of \( NN \)-dicyclohexylmethylamine, the amine base used for the dehydrobromination reaction. Therefore, careful distillation of the raw products was necessary to minimize the cyclohexene content. In the second reaction step the 1-alkenes were oxidized using 3-chloroperbenzoic acid. After distillative purification of the 1-alkene oxides no more than traces of other isomers were found. Cyclohexene oxide was present only in 1-hexene oxide-d\(_{12} \) at a level of about 0.25%. Other impurities found in 1-hexene oxide-d\(_{12} \) were ethanol, ethyl acetate, and ethyl formate, which most likely originated from the solvent diethyl ether and were accumulated in the distillation process. In addition, in 1-hexene oxide-d\(_{12} \) small quantities of chlorobenzene were found. This compound originates from the peracid used in the oxidation steps. Except the chlorobenzene the other impurities could be fully eliminated in the drying process of the monomers over CaH\(_2\). However, the small quantities of chlorobenzene of not more than 0.05% had no influence on the polymerization processes. The molecular weight distributions of the deuterated polymers were comparable to the ones of the hydrogenous polymers and the measured molecular weights coincided within the experimental error with the expected values calculated from the amounts of monomer and initiator used (cf. Table 1).

It is a standard procedure to fit the SANS data with the Debye approximation, i.e., eq 2 multiplied with the forward scattering \( I_0 \). Since PBO and PHO have relatively large degrees of polymerization, the Debye function can be used in these cases. As an example, Figure 1 shows the scattering curves of the three PHO mixtures on the absolute scale, measured at 300 K together with the Debye fits. The fits agree very well with the data points, which is true for both PBO and PHO, and all temperatures. This procedure yields the radius of gyration \( R_g \) of the minority component, which means in the present case that of the deuterated polymers. The \( R_g ' \)s showed no significant and systematic change with temperature and were thus taken to be independent of temperature within the small range we studied (280 to 320 K). Therefore, the values, which can be found in Table 3, are averaged over the three temperatures.

For the rather short POO, which has only roughly 80 monomers, the discrete scattering function of a Gaussian chain eq 1 has to be used. Exemplary curves are shown in Figure 2. Also here, the \( R_g \) of the deuterated component is obtained. Additionally fitting PBO and PHO with eq 1 produced the same \( R_g \) values as eq 2, thereby showing that the use of the Debye approximation is well justified in these cases.

The slopes at high \( Q \)-values are proportional to \( Q^2 \) with \( x = -2.0 \pm 0.1 \) for PBO, \( -1.9 \pm 0.1 \) for PHO, and \( -1.7 \pm 0.1 \) for...
Table 3. Temperature Averaged $R_g$'s of the Deuterated Components from the Debye and Zimm Plots, eq 1, and RPA, and $\chi$ from the Zimm Plots and RPA

<table>
<thead>
<tr>
<th></th>
<th>PBO</th>
<th>PHO</th>
<th>POO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_g$ [Å]</td>
<td>50.5 ± 0.1</td>
<td>42.8 ± 0.5</td>
<td>—</td>
</tr>
<tr>
<td>$R_g$ [Å]</td>
<td>50.5 ± 0.1</td>
<td>43.1 ± 0.5</td>
<td>23.26 ± 0.05</td>
</tr>
<tr>
<td>$\chi$ [mol/cm³]</td>
<td>53.7 ± 0.5</td>
<td>43.0 ± 0.5</td>
<td>23.2 ± 0.1</td>
</tr>
<tr>
<td>$\chi$ [mol/cm³]</td>
<td>(—) 2.25 ± 0.25 × 10⁻⁵</td>
<td>(—) 1.0 ± 0.5 × 10⁻⁵</td>
<td>(4.6 ± 3.3) × 10⁻⁵</td>
</tr>
<tr>
<td>$R_g$ [Å]</td>
<td>48.0 ± 0.5</td>
<td>40.2 ± 0.5</td>
<td>19.5 ± 0.5</td>
</tr>
<tr>
<td>$\chi$ [mol/cm³]</td>
<td>(4 ± 1) × 10⁻⁵</td>
<td>(5 ± 1) × 10⁻⁵</td>
<td>(29 ± 4) × 10⁻⁵</td>
</tr>
</tbody>
</table>

For all samples, the $\chi$ values for PBO and PHO, this corresponds to the Debye prediction, and also for short chains the obtained value is reasonable, because the slope expected from the full scattering function is smaller than $Q^{-2.26}$. In Figure 3, an exemplary Zimm plot (PBO@320 K) is shown. For all samples, the $Q$-range was chosen such that $QR_g \leq 1$. Being the low-$Q$ expansion of the Debye function, the Zimm analysis is independent of the chain statistics at high $Q$ and should therefore give reliable results for all PAO’s. The obtained radius of gyration and Flory–Huggins interaction parameters $\chi$ are listed in Table 3. The $R_g$ are again those of the deuterated component. The small values for $\chi$ indicate that the isotope interaction between protonated and deuterated polymer is insignificant.

Additionally, RPA fits according to eq 4 were performed. The radius of gyration of the deuterated component $R_g$ coupled to the protonated polymers' $R_g$ via the known ratio of monomer numbers $N_i = h_i, d_i$, so that $R_g = R_g(h_i/N_h/d_i)^{1/2}$. The different concentrations were fitted simultaneously, and again no significant and systematic change with temperature was observed. Hence also in this case $R_g$ and $\chi$ given in Table 3 are averaged over the three temperatures. The radii of gyration obtained from the RPA are uniformly a bit smaller than those from the other methods, while the $\chi$ values are somewhat larger. The latter, however, are again close to zero and it can thus be concluded that the above statement concerning the interspecies interaction holds. Because of the good quality of the fits, it is not possible to discern RPA and Debye fits by visual inspection, and therefore no additional picture is shown.

To judge the influence of the asymmetry in molecular weight of the protonated and deuterated components, a second RPA fit was done: the ratio of monomers was set to 1, and $\chi$ was fixed to the value obtained before. The resulting $R_g$ did not differ within the error-bars from the one where the correct ratio was used. Therefore, we conclude that the difference in the degree of polymerization is small enough that it has no effect on the fitting parameters.

The $R_g$ of POO has been measured before by Hamley et al.\textsuperscript{21} There, $R_g = 22.0 \pm 0.4$ Å independent of temperature (between 300 and 450 K) was obtained using $M_w(h) = 10100$ g/mol and $M_w(d) = 12150$ g/mol (this corresponds to an h-equivalent $M_w$ of 10800 g/mol), with a mixture of 5:95 h/d-POO (i.e., their $R_g$ is that of the protonated polymer). With these values, $(\langle R_g^2 \rangle/M) = 0.29 \pm 0.01$ Å$^2$ g/mol, which is within the errors equal to the value obtained in the present work.

Fetters and co-workers have examined the relation of the unperturbed chain dimensions of several poly(olefin)s to their molecular weight per backbone bond $m_0$.\textsuperscript{12} They found that this ‘backbone equivalence’ model (BE model) correctly shows that $(\langle R_g^2 \rangle/M)$ scales with $m_0$, but does not produce very exact values.

We have used an analogous expression for the PAO’s in ref 20 to get an idea of the chain dimensions and the entanglement molecular weight $M_e$. With the SANS measurements, it is now possible to calculate the same quantities based on experimental data, and thereby test the quality of the BE model for the POO’s.

In analogy to ref 12, the chain dimensions $(\langle R_g^2 \rangle/M)$ are calculated as a function of the dimensions of poly(ethylene oxide) (PEO)

$$\frac{\langle R_g^2 \rangle}{M} = \frac{m_0}{m_0} \left( \frac{\langle R_g^2 \rangle}{M} \right)_{\text{PEO}}$$

where $m_0 = 3m_b$ is the mass of a monomer.
The entanglement molecular weight $M_e$ can then be calculated by using

$$M_e = \left(\frac{n_f}{n_0}\right)^2 M_\infty \rho \frac{N\text{monob}}{N\text{backbone bond}}$$  (7)

$p$ is the so-called packing length\(^9\) (Witten et al.\(^{27}\) seem to be the first ones to have used this term for their parameter $a$, which differs from $p$ only by a factor of 3), and $n_f$ is the Ronca-Lin parameter, equal to the number of entanglement strands in a cube with a side length equal to the tube diameter.\(^{28,29}\) Taking into account the values we find in the literature,\(^9,27\) it seems justified to take $n_f = 20 \pm 1$. For PEO, $m_0 = 44$, and $\left(\left(\langle R^2 \rangle_0 \rangle \right)_{PEO} = 0.805 \text{ Å}^2 \text{ mol/g.}^{13}$ The latter value was to our knowledge obtained using $R_g$ from Zimm plots.

The derived values resulting from the SANS data (using $R_g$ from the Zimm plots) are listed in Table 4(a). For the calculation of $\left(\langle R^2 \rangle_0 \rangle / M \rangle_{PEO} = 0.805 \text{ Å}^2 \text{ mol/g.}^{13}$

The results of eq 6 and eq 7 are given in Table 4(b). The values for $p$, $M_e$, and $d_i$ are recalculated as compared to ref 20, since there $n_f = 19$ and the mass density $\rho$ at 273 K has been used.

One can see that the values for $\left(\langle R^2 \rangle_0 \rangle / M \rangle_{measurement$ and calculation agree very well within the error-bars. For the deduced values $p$, $M_e$, and $d_i$ experiment and calculation agree in most cases, or are close to each other. The largest deviations occur for POO, i.e. for the PAO with the longest side chain. We would like to emphasize that in all cases the correct tendency was predicted, and the absolute values are astonishingly close!

The small deviations become more visible when looking at the characteristic ratio $C_\infty$ which can be regarded as a measure of the stiffness of a polymer chain. $C_\infty$ can be written as (cf. eq 3)

$$C_\infty = \frac{6R_g^2}{N\text{monob}m_0^2} = \frac{\langle R^2 \rangle_0 m_0}{M} \left(\frac{1}{\langle \theta \rangle_0} \right)$$  (8)

For poly(alkylene oxide)\(_n\), $n_{\langle \theta \rangle_0} = 6.46 \text{ Å}^2$, and we obtain the values given in the last column of Table 4. Inserting eq 6 results in a constant $C_\infty = C_\infty(\text{PEO})$ for all PAO’s.

It is interesting that $\left(\langle R^2 \rangle_0 \rangle / M \rangle$ of the PAO’s decreases as $m_0$ increases in such a way that the resulting $C_\infty = \left(\langle R^2 \rangle_0 \rangle / M \rangle_{PEO}$ is only slightly increasing, whereas a completely different picture shows up for the poly(olefin)s, as visualized in Figure 4. While $C_\infty$ of the PAO’s is around the constant line obtained from the BE model, the poly(olefin)s show a fishhook-like behavior of $C_\infty$. This means that poly(propylene) and poly(ethylglycol) appear more flexible than poly(ethylene) but the higher homologues become increasingly stiff, while the PAO’s do have a similar flexibility for all side-chain lengths. For better orientation, a list of $m_0$ of the PAO’s and poly(olefin)s is given in Table 5.

The fact that $C_\infty$ changes less strongly for the PAO’s can be understood qualitatively by taking into account that their C—C—C backbone repeat unit is in itself more flexible than the C—C backbone of the poly(olefin)s. In a more hand-waving fashion, one could say that due to the oxygen atom there is more

Figure 4. $C_\infty$ vs the mass per backbone bond $m_0$ for poly(olefin)s (filled squares; data taken from ref 10) and PAO’s (empty circles). The value for PPO is calculated from ref 2. The line shows the value obtained from the BE model.

Table 5. Molecular Weight per Backbone Bond $m_0$ of PAO’s and Poly(olefin)s

<table>
<thead>
<tr>
<th>no. of C(^a)</th>
<th>PAO’s $m_0$ [g/mol]</th>
<th>poly(olefin)s $m_0$ [g/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>PEO</td>
<td>14.67</td>
</tr>
<tr>
<td>1</td>
<td>PPO</td>
<td>19.33</td>
</tr>
<tr>
<td>2</td>
<td>PBO</td>
<td>24.00</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>PHO</td>
<td>33.33</td>
</tr>
<tr>
<td>6</td>
<td>POO</td>
<td>42.67</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>PDO</td>
<td>61.33</td>
</tr>
</tbody>
</table>

\(^a\) Number of carbon atoms per side chain.
space for the side chains alongside the backbone in the case of the PAO’s, and the coiling of the chain is less inhibited than in the case of the poly(olefin)s.

Since the estimate was rather accurate, one can dare to give values for a PAO with even longer side chain: poly(dodecene oxide) (PDO) has 10 carbon atoms in each \( n \)-alkyl side chain, thus \( m_b \approx 61.33 \). The density of PDO at 310 K is \( \rho = 0.88 \) g/cm\(^3\), and with this the BE model gives \( \langle R_g^2 \rangle_0/M \approx 0.19 \) Å\(^2\) mol/g. The expected entanglement molecular weight is \( M_e \approx 200 \pm 20 \) kg/mol, and the packing length should be \( p \approx 9.8 \) Å. The latter makes PDO a highly interesting polymer, since it is expected that \( M_e \), the critical molecular weight \( M_c \) (i.e., where \( \eta_0 \approx M \) changes to \( \eta_0 \approx M^{1.4} \)), and the reptation molecular weight \( M_0 \), (i.e., where \( \eta_0 \approx M^{1.4} \) changes to \( \eta_0 \approx M^0 \)) coincide for polymers with \( p = p^* \approx 9.2 \) Å.\(^{10} \) This is visualized in Figure 5. In the picture of the tube model, this means that the contour-length fluctuation regime is missing and the limit of pure reptation is reached as soon as entanglements are present.

The packing length increases as a function of \( m_b \) as is shown in Figure 6. For the very short side chains, the slope is almost identical for the poly(olefin)s and the PAO’s, but then the poly(olefin)-values seem to saturate. The PAO-slope remains virtually unchanged (at least up to the estimated value for PDO) and follows the line that would be expected from the BE model using the appropriate densities. It has to be concluded that the BE model is by no means a perfect description of the static properties of side-chain polymers, but that, other than the poly(olefin)s, the PAO’s can be reasonably well approximated.

A possible explanation for the obviously different behavior of the poly(olefin)s and PAO’s may be given by the so-called generalized anomeric effect.\(^{30,31} \) It is commonly found that there is a much higher probability for gauche conformations when in a sequence of C atoms an atom with lone pair electrons is present. This is the case for the PAO’s, and it is therefore understandable that the radius of gyration depends only very little on temperature compared to polymers with pure carbon backbones: for instance it is found that \( R_g \) of poly(ethylene propylene) decreases by \( \approx 4\% \) when increasing the temperature by 100 K, the temperature coefficient being \( \kappa = -1.16 \times 10^{-3} \) K\(^{-1}\). This effect is attributed to the increased population of the gauche conformation with increased temperature. When the gauche conformation is now favored even at low temperatures, there may be either no change in \( R_g \) or it might also increase, depending on the shape of the rotation potential. For PEO, \( \kappa \) is found to be \( -3.0 \times 10^{-4} \) K\(^{-1}\), which is by far smaller than the PEP value. Hamley et al.\(^{21} \) found \( R_g \) of POO independent of temperature between room temperature and 178 °C. These findings indicate that the rotational potentials of the PAO’s are such that changes in temperature have almost no effect on the chain dimensions. Furthermore, the accessibility of many conformational states should make the chains more flexible and can therefore account for the rather small characteristic ratio.

## SUMMARY

We reported the synthesis of deuterated alkylene oxide monomers, and small-angle neutron scattering measurements on three different poly(alkylene oxide)s. The latter showed a systematic decrease of \( \langle R_g^2 \rangle_0/M \) with increasing length of the side chains, and concurred in an almost-quantitative fashion with the values obtained from the very simple backbone equivalence model.\(^{12,20} \) On the basis of the good agreement, a prediction of the chain properties of poly(dodecene oxide) is featured, giving reason for the assumption that this polymer has a packing length very close to the value where \( M_e = M_c = M_0 \) is expected. The qualitatively different behavior of the characteristic ratio of the poly(alkylene oxide)s and the poly(olefin)s is discussed in terms of the molecular mass per backbone bond and the generalized anomeric effect, which may give at least a qualitative reason for the observations.

## ASSOCIATED CONTENT

### Supporting Information

Table with all detected components after the hexenoxy synthesis and mass spectrum of hexenoxy-D12 with peak interpretation. This material is available free of charge via the Internet at http://pubs.acs.org.
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