

Supporting information

**Secondary structures formation of main-chain chiral
poly(2-oxazoline)s in solution.**

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1. SEC traces of poly-*R*-2-butyl-4-ethyl-2-oxazoline (p-*R*-BuEtOx), poly-*RS*-2-butyl-4-ethyl-2-oxazoline (p-*RS*-BuEtOx) and *S*-2-butyl-4-ethyl-2-oxazoline (p-*S*-BuEtOx).
2. Circular dichroism spectra of p-*S*-BuEtOx
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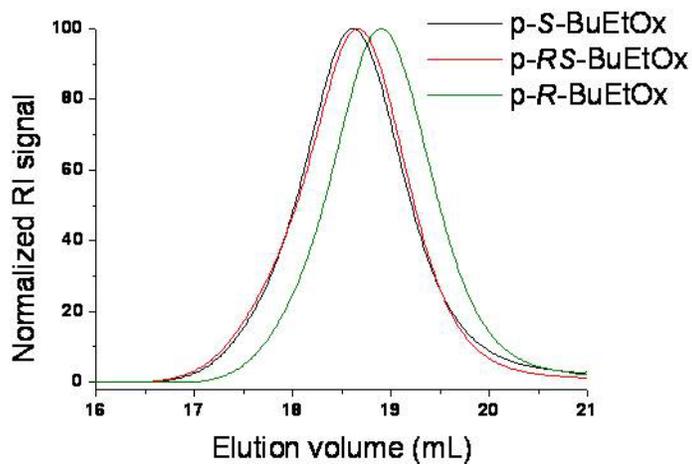


Figure 1: SEC traces obtained in dimethylacetamide.

2. Circular dichroism spectra of p-S-BuEtOx

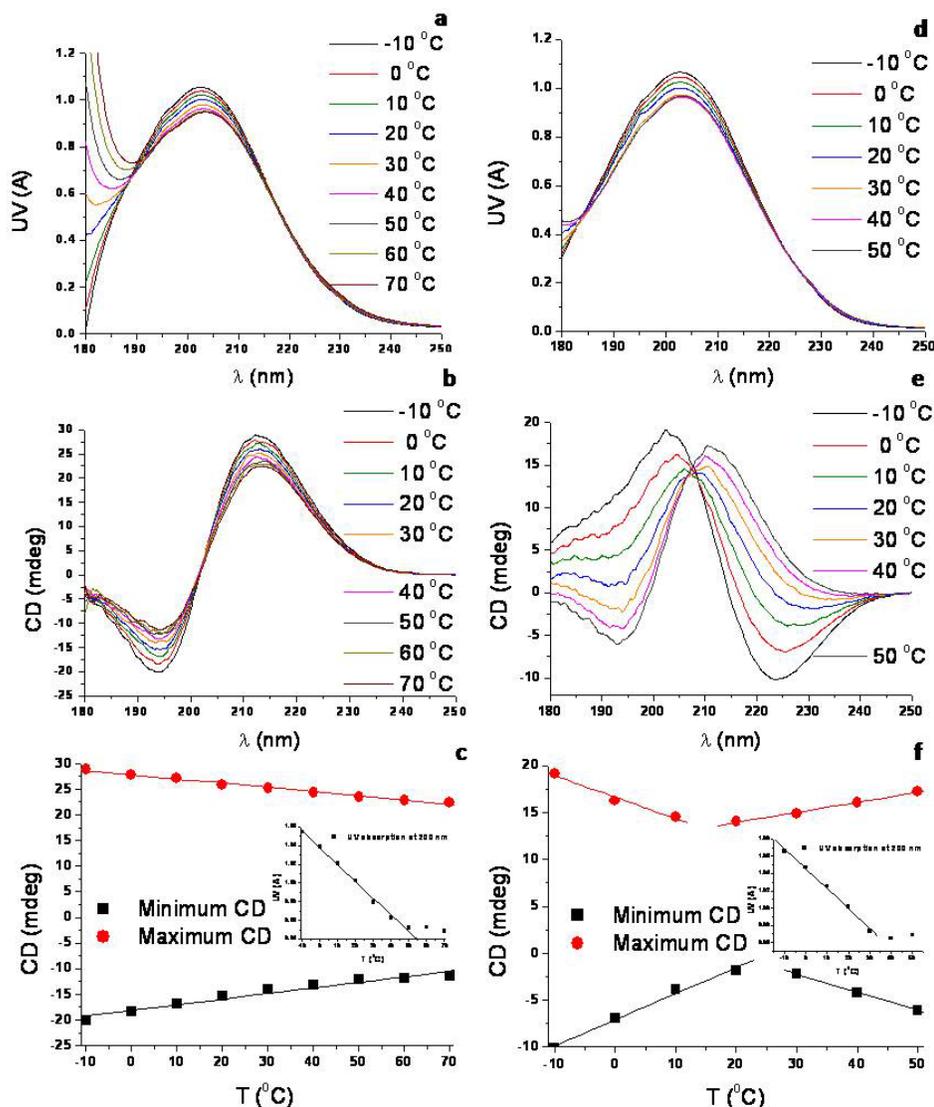


Figure 2 Left: Temperature dependence of the UV absorption (a) and the Cotton effects (b) of p-S-BuEtOx dissolved in TFE and linear decrease of the Cotton effects with the decrease in temperature (c) inset is linear decrease of UV-maximum with the decrease in temperature. **Right:** Temperature dependence of the UV absorption (d) and the Cotton effects (e) of p-S-BuEtOx dissolved in HFIP and linear decrease and increase of the Cotton effects with the decrease in temperature (f) inset is linear decrease of UV-maximum with the decrease in temperature.

3. Circular dichroism spectra of p-RS-BuEtOx

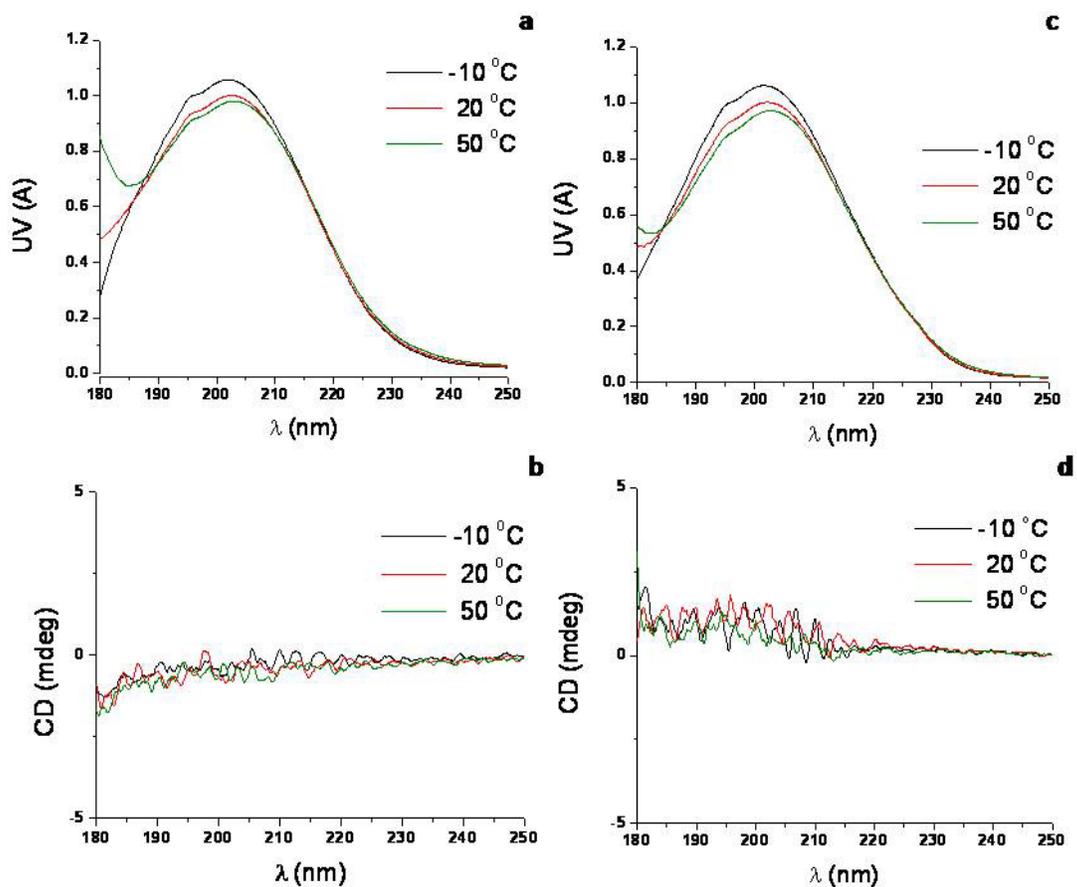


Figure 3 Left: Temperature dependence of the UV absorption (a) and the Cotton effects (b) of p-RS-BuEtOx dissolved in TFE. **Right:** Temperature dependence of the UV absorption (c) and the Cotton effects (d) of p-RS-BuEtOx dissolved in HFIP.

4. Theoretical considerations SANS measurements

The Guinier approximation relates to the low Q ($QR_g < 1$) part of the scattering plot providing the radius of gyration (R_g) of the particle. The normalized scattered intensity $I(Q)$ is given by the following expression:

$$I(Q) = N_p \Delta\rho^2 V_p^2 P(Q, R) S(Q)$$

where N_p is the number of particles in the sample, $\Delta\rho = \rho_p - \rho_m$, V_p is the volume of a particle, $P(Q, R)$ is the single particle form factor arising from the intra-particle scattering and $S(Q)$ is the structure factor which arises from inter-particle interactions.

At low Q (the Guinier regime) and in dilute non-interacting systems, $S(Q) = 1$ and therefore $P(Q, R)$ simplifies to the following:

$$P(Q, R) = 1 - \frac{Q^2 R_g^2}{3}$$

Assuming that $1 - X^2 \approx \exp(-X^2)$ the expression for $I(Q)$ then becomes:

$$I(Q) \approx N_p \Delta\rho^2 V_p^2 \exp\left(-\frac{Q^2 R_g^2}{3}\right)$$

Plotting a graph of $\ln[I(Q)]$ vs. Q^2 should give a linear section in the Guinier regime and the R_g can be obtained from the slope of this section:

$$Slope = -\frac{R_g^2}{3}$$

For the systems being examined in this study R_g is expected to be larger for an ordered structure when compared to a random coil.

A Kratky plot is obtained by plotting $I(Q).Q^2$ vs. Q and contains information on the conformation of the polymer molecules within a system. The graph consists of three distinct regimes (Figure 5): the low Q section consists of a steep rising slope and can be related to the R_g of the entire molecule, the steep gradient then decays into the intermediate (Debye) section which contains information on the random arrangement of the polymer chain elements. The tail section of the Kratky plot will again begin to increase with a steep slope, the start of which can be related to the persistence length of the molecule. A more compact or structured molecule will have a more pronounced peak at low Q when compared to a random coil whose form will be more like a plateau.¹

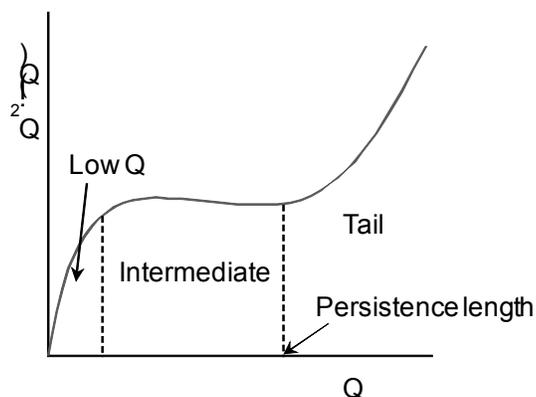


Figure 4: Schematic Kratky plot showing the three distinct regimes.

Mathematical modeling of the systems was performed using the multi-model FISH fitting program.²⁸ This program is based on an iterative least-squares algorithm and allows for various common scattering laws to be tested. The best structural parameters and a measure of the fit residuals are obtained. The models employed were not chosen at random; the general form factors of the obtained scattering curves were taken into account as were results from Guiner analyses and Kratky plots along with data from other techniques such as CD. Absolute intensities and scale factors were determined for each data set to ensure that the most suitable structural model had been chosen. The fitting analyses used for this data was either the ellipsoid form factor or a Gaussian coil model. There are two structural dimensions in the ellipsoid model; the primary and secondary radii, R_1 and R_3 with an aspect ratio $X = R_3/R_1$. The value of X is unity for a spherical, < 1 for an oblate (Figure 6(a)) and > 1 for a prolate (Figure 6(b)) structure.

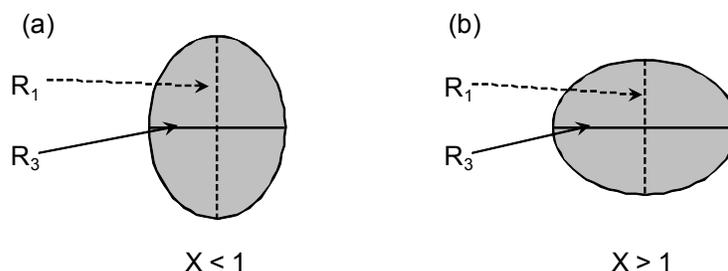


Figure 5: Schematic representation of the change in particle size with X .

Estimates of the limiting radii can be made from the length and structure of the polymer and although all three parameters were allowed to float during the fitting process the

values obtained were always kept within reason to these estimates. For an ellipsoidal particle the scale factor, S_F , is defined as:

$$S_F = \phi_p \Delta\rho^2 V_p$$

where ϕ_p is the volume fraction of particles, $\Delta\rho$ the scattering length density difference between the particle and the solvent and V_p is the volume of the particle. The volume is found using:

$$V_p = \frac{4}{3} \pi R^3 X$$

where R is the primary axis and X the axial ratio of the ellipsoid.

When using the Gaussian coil model, values for $I(0)$, flat background and the radius of gyration can be obtained. Again these parameters were allowed to float during fitting, but not allowed to become physically unrealistic (taking the polymer molar mass and structure into account, alongside results from Guinier analyses). For the Gaussian coil model employed, the absolute scattering intensity, $I(0)$, is given by:

$$I(0) = \phi \Delta\rho^2 V$$

where $\Delta\rho$ the scattering length density difference between the polymer and the solvent, ϕ = concentration of polymer (in $\text{g}\cdot\text{cm}^{-3}$) / density (in $\text{g}\cdot\text{cm}^{-3}$) and V is the volume of polymer in one scattering object (the coil), and is given by:

$$V = \frac{M_n}{d \cdot N_A}$$

where M_n is the molar mass of the polymer (in $\text{g}\cdot\text{mol}^{-1}$), d the density and N_A is Avogadro's constant.

ⁱ M. Kataoka, K. Kuwajima, F. Tokunaga and Y. Goto, *Protein Sci.* 1997, **6**, 422-430