Measurement of one nanometer polymer coil with Vasco Kin

Key Words: *Dynamic Light Scattering, polymer, polymer coils*

Abstract
This note presents the measurement of small polystyrene coils having a diameter close to one nanometer in toluene using the instrument "Vasco Kin".

Introduction

Dynamic Light Scattering is a powerful tool for the size characterization of nanoparticles dispersed in liquids. Based on the scattered light fluctuations induced by the Brownian motion of the particles, this technic give access to the whole nanometric range for a large panel of material while remaining fast and easy to operate. DLS is therefore a technic of choice for in situ and kinetic monitoring of suspensions, for example. Its capability to measure very small objects and suspensions at low concentration is also a great benefit in numerous applications like micelles, proteins, or other macromolecules characterization.

Short polymers chains belong to this category of objects difficult to characterize. When solubilized in good or theta solvent, these macromolecules form small "random coils" having a very low density, and, thus, law refractive index contrast with the continuous phase. As a consequence, only a little intensity of light is scattered by such sample and their characterization becomes even more challenging if the polymer coils have only few nanometer diameter.

In this note we present a measurement of small polystyrene coils in toluene using the instrument "Vasco Kin" showing that both the sensitivity and the resolution of the instrument allows to measure such low scattering particles down to the nanometer.

Material and protocol

The polymer studied here is a GPC standard polystyrene supplied by Sigma-Aldrich (ref 81402) and having a molecular weight (Mn) of 1020 Da and Mw/Mn=1.1.
This powder is diluted at 0.043g/mL (5%$_{wt}$) in pure toluene before being sonicated for 20 minutes using an ultrasonic bath.

The dynamic light scattering experiment is performed using "Vasco Kin" with its *in-situ* optical head in optical glass cuvette at 20°C (see figure 2). The correlogram processing is achieved using the SBL (for Sparse Bayesian Learning) inversion algorithm which provides sizes distributions for multimodal samples with a high level of resolution.
To decrease the impact of large impurities on such a low scattering polymer solution, an original functionality featured in Vasco kin software, and called "time slicing", is also applied on the raw light scattering data to "clean" the signal of its most inhomogeneous components.

Random polymer coils sizes can be estimated theoretically using scaling law. In our case, the molecular weight of only 1020Da is at the limit of such model validity. However, it can still be reasonably used to give an raw estimation of what result could be expected with DLS. Thus, assuming we are in the case of Gaussian coil in good solvent, we can calculate the gyration radius of the coil as[1]: $R_g = l.\left(\frac{n}{6}\right)^{0,6}.\sqrt{C_\infty}$ and the hydrodynamic radius: $R_h = \frac{R_g}{1.78}$, where l is the length of a c-c bond, n the polymer number of bonds (2 times the number of monomers in the case of polystyrene) and C_∞ the characteristic ratio of polystyrene in toluene.
Using $l = 0.154$ nm, n = 19.6, and $C_\infty = 9.5$ [2], we calculate a R_h of 0.543 nm i.e. an hydrodynamic diameter of **Dh= 1.086 nm.**

[1] R. J. Young & P. A. Lovell*, Introduction to polymers, 3rd Edition (CRC Press 2011).*

[2] K. Treao , N Morihana, H. Ichikaawa, Solution SAXS measurements over a wide temperature range to determine the unperturbed chain dimensions of polystyrene and a cyclic amylose derivative. *Polym. J.* **46,** 155-159 (2014).

Results

A reliable measurement of the polystyrene solution is achieved in less than 40 seconds acquisition.

The resulting correlogram is shown on figure 3.a. (blue dots) overlaid with the SBL algorithm fit (green line). The good correspondence between the fit and the experimental data is well illustrated by the low residues in yellow on the graph (less than 0.3% difference between the fit and the data). This solution calculated by SBL corresponds to the size distribution displayed, on figure 3.b weighted in intensity and, on figure 3.c weighted in particles number.

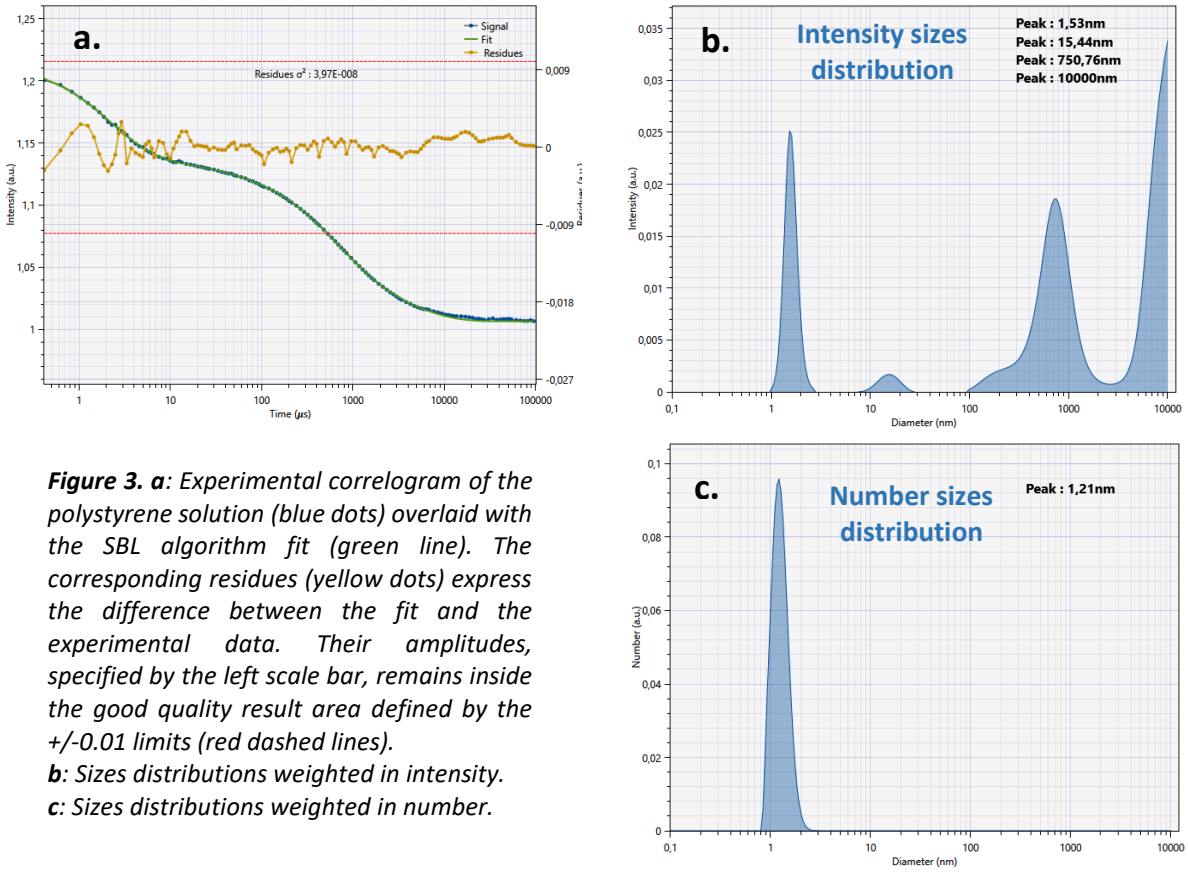

***Figure 3. a**: Experimental correlogram of the polystyrene solution (blue dots) overlaid with the SBL algorithm fit (green line). The corresponding residues (yellow dots) express the difference between the fit and the experimental data. Their amplitudes, specified by the left scale bar, remains inside the good quality result area defined by the +/-0.01 limits (red dashed lines).*
***b**: Sizes distributions weighted in intensity.*
***c**: Sizes distributions weighted in number.*

The size distribution in intensity (figure 3.b) shows that several populations are detected in the sample. In particular, we clearly observe a population having a hydrodynamic diameter of **1.53nm** (peak mode), consistent with the expected size range for such polystyrene coils in toluene.

Larger objects are also detected, and especially, a wide distribution of objects having a diameter from 100 nm to few tens microns likely to be large residual impurities (some dusts for instance). Even in low amount, such particles are responsible for an important part of the total light scattered by the sample due to their large sizes in comparison to the one of polystyrene coils. However, by converting the result in number weighted size distribution (figure 3.c.), it appears that the smaller population is in large majority in the sample (more than 99% in term of number of particles). The corrected hydrodynamic diameter of is then determined at **1.21nm**.

This result is very really close to the raw estimation of 1.086 nm calculated above. It shows that the Vasco kin can characterize a one nanometer polystyrene coils in toluene with a good accuracy even in presence of some large impurities. Such challenging measurement demonstrates both the high sensitivity of the instrument and the quality of its data processing algorithm.

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