

# Supporting Information

to

## Self assembly and structural analysis of multiblock polyoxyalkylene copolymers

*Martin Dulle<sup>a</sup>, Muhammad I. Malik<sup>a,b</sup>, Bernd Trathnigg<sup>a,b</sup>, and Otto Glatter<sup>a,\*</sup>*

<sup>a</sup> Institute of Chemistry, Karl Franzens University, Heinrichstrasse 28, A-8010 Graz, Austria.

<sup>b</sup> Central Polymer Laboratories / Molecular Characteristics (CePOL / MC), Karl Franzens University,  
Heinrichstrasse 28, A-8010 Graz, Austria.

Fax +433163809850, e-mail: [otto.glatter@uni-graz.at](mailto:otto.glatter@uni-graz.at)

**Dynamic light scattering (DLS):** All samples were measured at 0.1 or 1 wt%, depending on the turbidity of the solutions in 1.5 ml glass vials at 25°C. The DLS equipment is composed of a goniometer and a diode laser (Coherent Verdi V5,  $\lambda = 532$  nm,  $P_{max} = 5$  W) with single-mode fiber detection optics (OZ from GMP, Zürich, Switzerland), an ALV/SO-SIPD/DUAL photomultiplier with pseudo cross correlation and an ALV 5000/E correlator with fast expansion (ALV, Langen, Germany). Measurements were carried out at a scattering angle of 90°. Correlation functions were collected for 60 seconds ten times, and then averaged. From these functions, the average diffusion coefficient  $D$  was obtained by cumulant analysis. In this method, the correlation function is expanded in a power series, where the expansion coefficients (cumulants) correspond to the moments of the intensity distribution. The first cumulant is the mean of the distribution, and the second is the variance or width of it. The first cumulant gives the z-average of the diffusion coefficient  $D$ . This diffusion coefficient  $D$  is related to the hydrodynamic radius  $R_H$  through the Stokes–Einstein equation:

$$R_H = \frac{k_B T}{6\pi\eta D} \quad (1)$$

where  $k_B$  is the Boltzmann constant,  $T$  the absolute temperature and  $\eta$  the viscosity of the solvent. The hydrodynamic radius is the radius of a compact sphere with the diffusion coefficient  $D$ . Another source of information, especially concerning polydisperse systems, is to carry out a Laplace inversion with the program ORT<sup>19</sup>. The intensity weighted size distributions were calculated as for those no further assumptions about the system have to be made. On the other hand, intensity distributions are very sensitive to large aggregates, because the scattered intensity increases with  $\sim r^6$  for globular particles.

**Small-angle X-ray scattering (SAXS):** The amphiphilic block copolymer samples that formed small enough aggregates (< 40 nm) were evaluated with small-angle X-ray scattering (SAXS). The SAXS equipment is composed of a SAXSess camera (Anton Paar, Austria) attached to an X-ray generator (Philips, PW 3830) with a sealed-tube anode (Cu- $K_\alpha$  wavelength of 0.154 nm). The generator was operated at 40 kV and 50 mA. The SAXSess camera is equipped with focusing multilayer optics and a block collimator for an intense and monochromatic primary beam with low background. A semi-

transparent beam stop enables measurement of an attenuated primary beam for the exact definition of the zero scattering vector and transmission correction. Samples were enclosed in vacuum-tight, reusable 1 mm quartz capillary tubes in order to obtain constant scattering volume and background contribution. The sample temperature was controlled with a thermostatted sample holder unit (TCS 120, Anton Paar). The 2D scattering pattern was recorded with imaging plates, or with a CCD detector, and integrated into a one-dimensional scattering function with SAXSQuant software from Anton Paar, Graz, Austria. The image-plate reader was a Fuji BAS1800 (from Raytest, Straubenhardt, Germany). The CCD camera, from Princeton Instruments, which is a division of Roper Scientific Inc. (Trenton, NJ, USA), is equipped with a PI-SCX fused fiber 1:1 optic taper. The CCD camera features a 2048\*2048 array with a pixel size of 24\*24  $\mu\text{m}$  (chip size: 50\*50 mm) at a sample–detector distance of 311 mm. All 2D scattering patterns were converted to one-dimensional scattering curves as a function of the magnitude of the scattering vector  $q = (4\pi/\lambda)\sin(\theta/2)$ , where  $\theta$  is the total scattering angle. All scattering patterns were transmission corrected by adjusting the attenuated scattering intensity at  $q = 0$  to unity, and correcting for the scattering of the sample cell and the solvent. In order to obtain the scattering patterns on an absolute scale, water was used as a secondary standard<sup>1</sup>. Samples were equilibrated at 25°C for 10 min before each measurement. The samples were exposed to X-rays for three 15 min periods, and the integrated scattering profiles were averaged.

**Determination of aggregation numbers:** The aggregation number of a micelle can be easily calculated via the molecular weight of the micelle if the average molecular weight of a single polymer molecule is known<sup>2</sup>, according to equation 2;

$$M = \frac{d\Sigma(0)}{d\Omega} \left( N_A / c \Delta\rho_M^2 \right) \quad (2)$$

where  $M$  is the molecular weight,  $\frac{d\Sigma(0)}{d\Omega}$  ( $\text{cm}^{-1}$ ) is the forward scattering intensity at  $q = 0$ ,  $c$  ( $\text{g}/\text{cm}^3$ ) is the polymer concentration,  $N_A$  is the Avogadro number, and  $\Delta\rho_M$  ( $\text{cm}/\text{g}$ ) is the scattering-length difference per mass:

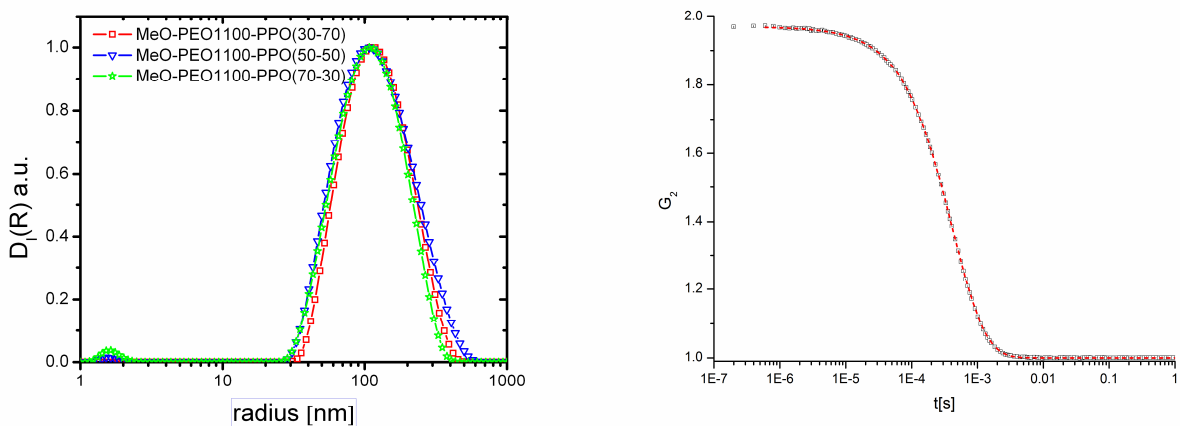
$$\Delta\rho_M = \Delta\rho \times \bar{v} \quad (3)$$

Once the chemical composition of the polymer and solvent is known, the scattering-length difference  $\Delta\rho$  (cm<sup>-2</sup>) can be calculated. Density measurements of solvent and polymer solutions, which were performed in our laboratory with a DMA 5000 (Anton Paar), were used to calculate the specific volume of the polymer in solution  $\bar{v}$  (cm<sup>3</sup>/g).

**SAXS data evaluation:** The scattering patterns were evaluated using the indirect Fourier transformation (IFT)<sup>3</sup> method. With this technique, the scattering curves can be interpreted in real space, and are represented by a pair-distance distribution function (PDDF). The PDDF is the Fourier transform of the angle-dependent scattering intensity. It represents a histogram of the distances inside the particle weighted with the electron-density differences in the solvent, and becomes zero at the maximum particle dimension<sup>4</sup>. The PDDF is the convolution square of the electron-density distribution. The radially averaged electron density across the micelles was obtained by deconvolution of the PDDF by using the program DECON<sup>5,6,7</sup> with the assumption of spherical symmetry. This electron-density profile yields information about the size of the domains within the micelles.

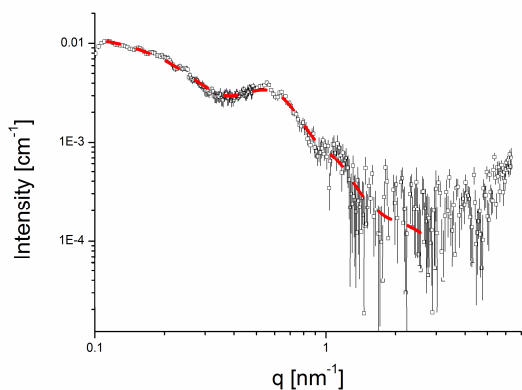
# Data

## EO-PO diblock copolymers



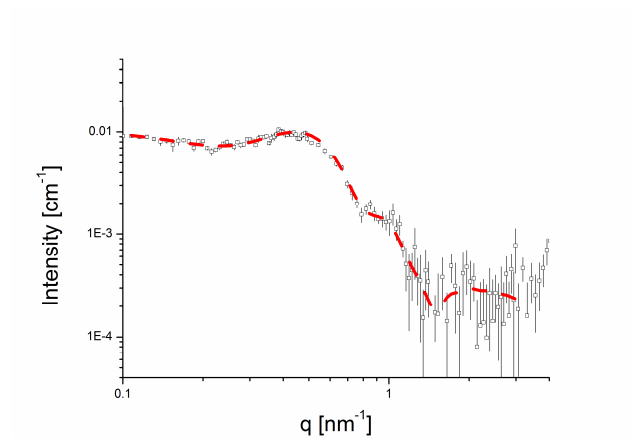
**Figure 1: DLS**, left: Intensity-weighted size distributions for the MeO-PEO1100-PPO block copolymers (sample nr. 1, 2 and 3 in Table 1) right: The autocorrelation function of sample nr. 2 and the fit from ORT of the size distribution

## EO-BO diblock copolymers

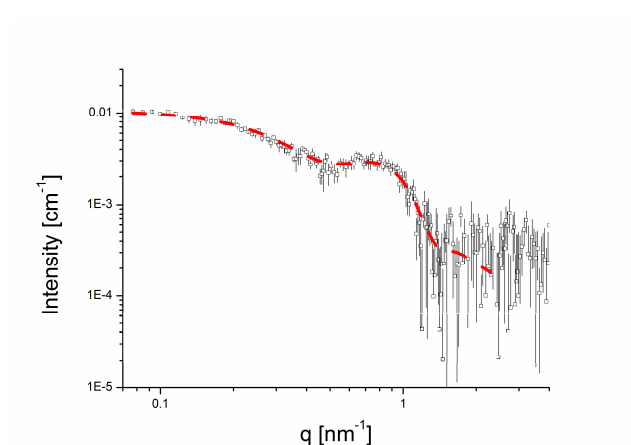


**Figure 2: SAXS**, ( $\square$ ) Scattering curve of MeO-PEO1100-PBO (50-50) block copolymer (sample Nr.5), and the fit (—) from the IFT

## EO-HO diblock copolymers

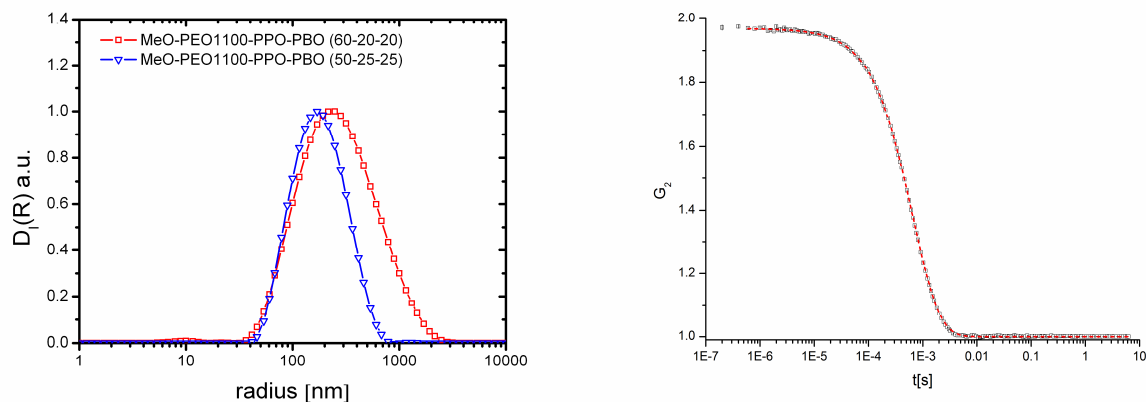


**Figure 3: SAXS, ( $\square$ )** Scattering curve of MeO-PEO1100-PHO (50-50) block copolymer(sample Nr.8), and the fit (**— —**) from the IFT



**Figure 4: SAXS, ( $\square$ )** Scattering curve of MeO-PEO1100-PHO (70-30) block copolymer(sample Nr.9), and the fit (**— —**) from the IFT

## Tri-block copolymers (EO-PO-BO)



**Figure 5: DLS,** left: Intensity-weighted size distributions for the MeO-PEO1100-PPO-PBO tri-block copolymers (samples 10 and 11 in Table 1) right: The autocorrelation function of sample nr. 10 and the fit from ORT of the size distribution

## References and Notes

- (1) Schnablegger, H.; Glatter, O.; *Applied Optics* **1991**, 30, 4889-4896
- (2) Orthaber, D.; Bergmann, A.; Glatter, O.; *J. Appl. Crystallogr.* **2000**, 33, 218.
- (3) Glatter, O.; *J. Appl. Crystallogr.* **1977**, 10, 415-421.
- (4) Glatter, O.; *J. Appl. Crystallogr.* **1979**, 12, 166-175.
- (5) Glatter, O.; *J. Appl. Crystallogr.* **1981**, 14, 101.
- (6) Glatter, O.; Hainisch, B.; *J. Appl. Crystallogr.* **1984**, 17, 435.
- (7) Mittelbach, R.; Glatter, O.; *J. Appl. Crystallogr.* **1998**, 31, 600.