Supporting Information for

# Effect of Pressure on the Micellar Structure and Aggregation Behavior of PMMA-*b*-PNIPAM Diblock Copolymers in a Water/Methanol Mixture

Pablo A. Alvarez Herrera,<sup>a</sup> Feifei Zheng,<sup>a</sup> Peiran Zhang,<sup>a</sup> Julija Reitenbach,<sup>b</sup> Heinz Amenitsch,<sup>c</sup> Cristiane Henschel,<sup>d</sup> André Laschewsky,<sup>d,e</sup> Peter Müller-Buschbaum,<sup>b</sup> Alfons Schulte,<sup>f</sup> and Christine M. Papadakis<sup>a\*</sup>

<sup>a</sup>. Technical University of Munich, TUM School of Natural Sciences, Physics Department,

Soft Matter Physics Group, James-Franck-Str. 1, 85748 Garching, Germany

<sup>b</sup>. Technical University of Munich, TUM School of Natural Sciences, Physics Department,

Chair for Functional Materials, James-Franck-Str. 1, 85748 Garching, Germany

<sup>c</sup>.Institute of Inorganic Chemistry, NAWI Graz, Graz University of Technology,

Stremayrgasse 9, 8010 Graz, Austria

<sup>*d*</sup>.Universität Potsdam, Institut für Chemie, Karl-Liebknecht-Straße 24-25, 14476 Potsdam-Golm, Germany

<sup>e</sup>.Fraunhofer Institute for Applied Polymer Research, Geiselbergstraße 69, 14476 Potsdam-Golm, Germany

<sup>f</sup>. University of Central Florida, Department of Physics and College of Optics and Photonics,

4111 Libra Drive, Orlando, Florida 32816, U.S.A.

## Chemical structure of PMMA21-b-PNIPAM283



Scheme 1. Chemical structure of PMMA<sub>21</sub>-*b*-PNIPAM<sub>283</sub>.

#### **Equations Used for Modeling the SAXS Data**

The Porod term  $I_P(q)$  is given by the following expression:<sup>1</sup>

$$I_{\rm P}(q) = \frac{I_{\rm P,0}}{q^m} \tag{S1}$$

where  $I_{P,0}$  is the scaling factor and *m* the Porod exponent.

The form factor of monodisperse core-shell spheres,  $P_{CS}(q)$ , is given by:<sup>2</sup>

$$P_{\rm CS}(q) = \left[ \left( \left( (1-\Phi)\eta_{\rm PNIPAM} + \Phi\eta_{\rm sol} \right) - \eta_{\rm sol} \right) \frac{4}{3} \pi R_{\rm m}^{3} A_{\rm s}(R_{\rm m},q) - \left( \left( (1-\Phi)\eta_{\rm PNIPAM} + \Phi\eta_{\rm sol} \right) - \eta_{\rm PNIPA} \right) \frac{4}{3} \pi R_{\rm c}^{3} A_{\rm s}(R_{c},q) \right]^{2}$$

$$\tag{S2}$$

where  $\Phi$  is the volume fraction of the solvent in the shell,  $R_{\rm m}$  is the micellar radius, namely,  $R_{\rm m} = R_{\rm c} + \Delta R$ , where  $R_{\rm c}$  and  $\Delta R$  are the core radius and the shell thickness, respectively.  $\eta_{\rm PNIPAM} = 10.25 \times 10^{-4} \,\rm nm^{-2}$ ,  $\eta_{\rm PMMA} = 10.82 \times 10^{-4} \,\rm nm^{-2}$  and  $\eta_{\rm sol} = 9.25 \times 10^{-4} \,\rm nm^{-2}$  are the scattering length densities (SLDs) of dry PNIPAM, PMMA and the solvent. The latter was calculated using the volume fractions and SLDs of D<sub>2</sub>O ( $\eta_{\rm D2O} = 9.44 \times 10^{-4} \,\rm nm^{-2}$ ) and CD<sub>3</sub>OD ( $\eta_{\rm CD3OD} = 7.54 \times 10^{-4} \,\rm nm^{-2}$ ). Finally,  $A_{\rm s}(R,q)$  is the scattering amplitude of a sphere of radius *R*:

$$A_{\rm s}(R,q) = \frac{3[\sin(qR) - qR\cos(qR)]}{(qR)^3}$$
(S3)

The polydispersity of the core radius  $R_c$  is modeled by the Schulz-Zimm distribution  $SZ_n(r,N,R_c,k)$ , which is given by:<sup>3</sup>

$$SZ_n(r, R_c, k) = \frac{1}{R_c} \left(\frac{r}{R_c}\right)^{k-1} \frac{k^k \exp(-kr/R_c)}{\Gamma(k)}$$
(S4)

with  $k = R_c^2/\sigma^2$ , where  $\sigma$  denotes the standard deviation of the distribution,  $\Gamma(x)$  is the Gamma function, and *r* the radial coordinate.

Accordingly, the form factor of polydisperse core-shell spheres  $I_{cs}(q)$  reads:

$$I_{cs}(q) = \int_0^\infty SZ_n(r, R_c, k) P_{cs}(q, r, R_c, \Delta R, \phi) dr$$
(S5)

To model the spatial correlation between the micelles, the Percus-Yevick hard-sphere structure factor  $S_{\text{HS}}(q)$  was used:<sup>4</sup>

$$S_{HS}(q) = \frac{1}{1 + 24f_S G(2R_{HS}q)/2R_{HS}q}$$
(S6)

where

$$G(x) = \gamma \frac{\sin x - x \cos x}{x^2} + \delta \frac{2x \sin x + (2 - x^2) \cos x - 2}{x^3} + \varepsilon \frac{-x^4 \cos x + 4(3x^2 - 6\cos x + (x^3 - 6x) \sin x + 6)}{x^5}$$
(S7)

with

$$\gamma = \frac{(1+2f_s)^2}{(1-f_s)^4}, \ \delta = \frac{-6f_s(1+f_s/2)^2}{(1-f_s)^4}, \ \varepsilon = \frac{\gamma f_s}{2}$$
(S8)

where  $R_{\rm HS}$  and  $f_{\rm s}$  are the hard-sphere radius and volume fraction, respectively.

The Ornstein-Zernike structure factor,  $I_{OZ}(q)$ , reads:<sup>5</sup>

$$I_{OZ}(q) = \frac{I_{OZ,0}}{1 + q^2 \xi^2}$$
(S9)

where  $I_{OZ,0}$  is the scaling factor of the Ornstein-Zernike structure factor, and  $\xi$  is the correlation length.

The Guinier-Porod model  $I_{GP}(q)$  reads:<sup>6</sup>

$$I_{GP}(q) = I_G \exp\left(\frac{-q^2 R_g^2}{3}\right) \quad \text{for } q \le q^*$$
(S10)

$$I_{GP}(q) = \frac{I_{P,0}}{q^m} \qquad \text{for } q \ge q^* \tag{S11}$$

where  $R_g$  is the radius of gyration of the particles (aggregates), *m* is the Porod exponent, and  $I_G$ and  $I_{P,0}$  are the Guinier and Porod scale factors, respectively. The following relations are obtained by the condition that the Guinier and Porod terms and their respective slopes are continuous at  $q^*$ :

$$q^* = \frac{1}{R_g} \left(\frac{3m}{2}\right)^2 \tag{S12}$$

$$I_p = I_G \exp\left(\frac{-m}{2}\right) \left(\frac{3m}{2}\right)^{\frac{m}{2}} \frac{1}{R_g^m}$$
(S13)

To fit the SAXS curves, the error function  $\chi^2$  was minimized.  $\chi^2$  is defined as:

$$\chi^2 = \sum_{i=1}^{N} \left( \frac{I^{exp}(q_i) - I^{mod}(q_i)}{\varepsilon_i} \right)^2$$
(S14)

where  $I^{\exp}(q_i)$  is the experimental scattering intensity,  $I^{\text{mod}}(q_i)$  is the scattering intensity given by the model,  $\epsilon_i$  is the experimental uncertainty of  $I^{\exp}(q_i)$ , and N is the number of data points.

## Determination of the Coexistence Line of PMMA<sub>21</sub>-*b*-PNIPAM<sub>283</sub> in D<sub>2</sub>O

Figures S1a and b present the temperature dependence of the normalized light transmission of the polymer in neat D<sub>2</sub>O at pressures between 10 and 150 MPa, and the corresponding  $T_{cp}$ -values in the temperature pressure frame, respectively. The  $T_{cp}$ -values are fitted by a parabola, which reads:

$$T = a(p - p_{\max})^2 + T_{\max}$$
 (S15)

where  $p_{\text{max}}$  and  $T_{\text{max}}$  are the pressure and temperature of the maximum of the parabola, and *a* is a negative constant.



Figure S1. (a) Normalized light transmission of a 3 wt % solution of PMMA<sub>21</sub>-*b*-PNIPAM<sub>283</sub> in  $D_2O$  as a function of temperature measured during heating scans at the pressures indicated in the

graph. (b) Resulting cloud points (symbols). The red solid line is the fit of the data by a parabola (eq. S15).

#### SAXS Data of the Pressure Scans with Corresponding Model Fits

In this section, the SAXS data at all pressures with their model fits are presented for the pressure scans at the four temperatures. The data are fitted in the *q*-range between 0.09 and 2.0 nm<sup>-1</sup>, and good agreement was obtained in most of the data. The curves in the one-phase region far away from the coexistence line differ slightly from the model for *q*-values larger than 0.4 nm<sup>-1</sup>. Possibly, concentration fluctuations due to a varying PNIPAM concentration along the micellar shell cause excess scattering in this *q*-range, which could not be accurately modeled using eq. 1. However, using a form factor with varying PNIPAM concentration in the shell, i.e., a model with more fit parameters, is discarded due to the possibility of overfitting the data and lower accuracy when comparing fitting parameters obtained from different models.

Also, the model differs from the data in the *q*-range between 0.09 and 0.2 nm<sup>-1</sup> in the curves in the two-phase region, i.e., at pressures higher than 200 MPa. In this *q*-range, the Porod term and the combined contribution of the form and structure factors dominate the intensity. The discrepancy between the data and the model may arise from the contributions of the Porod term  $I_P(q)$  or the structure factor  $S_{HS}(q)$ . Possibly, the surface roughness of the aggregates and/or the correlation between the micelles are not adequately described at these pressures. A possible reason might be the emergence of attractive interactions between the correlated micelles, requiring the use of a different structure factor, or the formation of fractal clusters by the micelles, which are not well described by the Porod form factor. In spite of these shortcomings, we decided to keep the model as simple as possible.



**Figure S2.** SAXS data of the polymer solution (vertically shifted, symbols) with model fits (solid black lines) at 28 °C. The shift factor ranges between  $10^1$  and  $10^2$ . Here, and in Figures S3-S5, the SAXS curves in the one-phase and two-phase region are colored bluish and reddish, respectively.



**Figure S3.** SAXS data of the polymer solution (vertically shifted, symbols) with model fits (solid black lines) at 30 °C. The shift factor ranges between  $10^1$  and  $10^2$ .



**Figure S4.** SAXS data of the polymer solution (vertically shifted, symbols) with model fits (solid black lines) at 31 °C. The shift factor ranges between  $10^1$  and  $10^2$ .



**Figure S5.** SAXS data of the polymer solution (vertically shifted, symbols) with model fits (solid black lines) at 36 °C. The shift factor ranges between  $10^1$  and  $10^2$ .

#### Fit Parameters from the Pressure Scan at 30 °C

In this section, the fit parameters of the pressure scan at 30 °C are presented and described. Figure S6a shows the structural parameters of the single micelles. In the one-phase region,  $R_c$  decreases steadily with pressure from 4.4 to 3.2 nm as pressure is raised to 100 MPa and remains roughly at this value up to 200 MPa.  $\Delta R$  initially increases from 4.6 to 7.6 nm up to 100 MPa and decreases to 6.1 nm as pressure is increased further to 200 MPa. As a result,  $R_m$  exhibits non-monotonic behavior. The micelles do not feature any spatial correlation ( $f_s = 0$ ) at pressures equal to or below 175 MPa (Figure S6b). Consequently, we cannot determine  $R_{\rm HS}$  in this pressure range. Figure S6c shows the volume fraction in the micellar shell.  $\Phi$  initially increases from 0.90 to 0.94 up to 100 MPa and remains constant as pressure increases further within the one-phase region. After crossing the coexistence line,  $R_c$  remains roughly constant at ca. 3.3 nm, while  $\Delta R$  diminishes to 4.1 nm at 250 MPa, which leads to a reduction of  $R_m$ . The difference between  $R_m$  and  $R_{\rm HS}$  increases with pressure in the two-phase region. This behavior was also observed at 28 °C.  $f_s$  substantially increases to 0.30 while  $\Phi$  decreases to 0.89 as pressure is increased up to 250 MPa. A similar behavior was observed in the two-phase region at 28 °C.



**Figure S6.** (a) Structural parameters from model fit of the SAXS data of the polymer solution for the pressure scan at 30 °C. Core radius  $R_c$ , shell thickness  $\Delta R$ , micellar radius  $R_m$ , and hard-sphere radius  $R_{HS}$  are given. (b) Volume fraction of the correlated micelles,  $f_s$ . (c) Volume fraction of the solvents in the micellar shell,  $\Phi$ . The light-blue region (a-c) indicates the one-phase region as determined from the structural parameters.

# Fit Parameters from Model Fits to the SAXS Data

<i>p</i> [MPa]	$I_{\mathrm{P},0}[\mathrm{a.u}]$	т	$I_0 \times 10^3$ [a.u]	σ	<i>I</i> <sub>OZ,0</sub> [a.u]	ζ[nm]	Ibkg [a.u]
10	0.014±0.001	3.90±0.10	23±1	0.15 <sup>f</sup>	2.30±0.20	0.70 <sup>f</sup>	0.10 <sup>f</sup>
25	0.016±0.001	3.90±0.10	23±1	0.15 <sup>f</sup>	2.60±0.20	0.70 <sup>f</sup>	0.10 <sup>f</sup>
50	0.015±0.001	3.80±0.10	23±1	0.15 <sup>f</sup>	2.50±0.25	0.70 <sup>f</sup>	0.10 <sup>f</sup>
75	0.014±0.001	4.00±0.10	22±1	0.15 <sup>f</sup>	2.30±0.20	0.70 <sup>f</sup>	0.10 <sup>f</sup>
100	0.010±0.001	4.05±0.05	21±1	0.15 <sup>f</sup>	2.10±0.20	0.70 <sup>f</sup>	0.10 <sup>f</sup>
125	0.006±0.002	4.30±0.05	22.5±0.5	0.15 <sup>f</sup>	2.10 <sup>f</sup>	0.70 <sup>f</sup>	0.10 <sup>f</sup>
150	0.006±0.002	4.25±0.05	21±1	0.15 <sup>f</sup>	1.90±0.20	0.70 <sup>f</sup>	0.10 <sup>f</sup>
175	0.004±0.002	4.45±0.05	22±1	0.15 <sup>f</sup>	1.60±0.20	0.70 <sup>f</sup>	0.10 <sup>f</sup>
200	0.003±0.001	4.60±0.05	19±1	0.15 <sup>f</sup>	1.30±0.20	0.70 <sup>f</sup>	0.10 <sup>f</sup>
225	0.035±0.005	3.80±0.10	20.5±0.5	$0.00^{\rm f}$	0.91±0.05	0.60 <sup>f</sup>	0.10 <sup>f</sup>
250	0.025±0.001	3.20±0.05	20±1	$0.00^{\mathrm{f}}$	0.70±0.10	0.70 <sup>f</sup>	0.10 <sup>f</sup>

Table S1. Fit parameters for the pressure scan at 28  $^{\circ}\mathrm{C}$ 

(a) Here, and in Tables S2-S4, the superscript "*f*" indicates that the variable was fixed during the

fits and a.u denotes arbitrary units.

<i>p</i> [MPa ]	$I_{\mathrm{P},0}[\mathrm{a.u}]$	т	$I_0 \times 10^3$ [a.u]	σ	$I_{\mathrm{OZ},0}$ [a.u]	ζ[nm]	<i>I</i> <sub>bkg</sub> [a.u]
10	0.010±0.005	4.00±0.10	17±1	0.15 <sup>f</sup>			0.60±0.2
25	0.010±0.005	4.10±0.10	15.5±0.5	0.15 <sup>f</sup>	1.30±0.20	$0.70^{\mathrm{f}}$	$0.20^{\rm f}$
50	0.004±0.001	3.90±0.10	16±1	0.15 <sup>f</sup>	1.30±0.20	$0.70^{\mathrm{f}}$	0.10 <sup>f</sup>
75	0.003±0.001	4.30±0.10	19±1	0.15 <sup>f</sup>	1.20±0.20	$0.80^{\mathrm{f}}$	0.10 <sup>f</sup>
100	0.002±0.001	4.40±0.10	25±1	0.15 <sup>f</sup>	0.70±0.20	$0.90^{\mathrm{f}}$	0.30 <sup>f</sup>
125	0.003±0.001	4.45±0.05	22±1	0.15 <sup>f</sup>	1.10±0.20	$0.80^{\mathrm{f}}$	0.10 <sup>f</sup>
150	0.005±0.002	4.50±0.10	21±1	0.15 <sup>f</sup>	1.10±0.20	$0.80^{\mathrm{f}}$	$0.10^{\rm f}$
175	0.004±0.001	4.60±0.10	21±1	0.15 <sup>f</sup>	0.90±0.20	$0.80^{\mathrm{f}}$	$0.10^{\rm f}$
200	0.003±0.001	4.70±0.10	20±1	0.15 <sup>f</sup>	0.60±0.10	0.60±0.10	$0.10^{\rm f}$
225	0.003±0.001	4.30±0.05	25±1	0.00 <sup>f</sup>			$0.20^{\rm f}$
250	0.005±0.005	3.90±0.05	21±1	0.00 <sup>f</sup>			0.30 <sup>f</sup>

Table S2. Fit parameters for the pressure scan at 30  $^{\circ}\mathrm{C}$ 

<i>p</i> [MPa]	I <sub>G</sub> [a.u]	$R_{\rm g}$ [nm]	т	Ibkg [a.u]			
10	$1.6 \times 10^{6} \pm 2.0 \times 10^{5}$	108±0.5	3.24±0.02	0.23±0.01			
<i>p</i> [MPa]	$I_{\mathrm{P},0}\left[\mathrm{a.u}\right]$	т	$I_0 \times 10^3$ [a.u]	σ	$I_{\mathrm{OZ},0}$ [a.u]	ζ[nm]	I <sub>bkg</sub> [a.u]
25	0.014±0.002	4.30±0.05	12.5±0.5	0.15 <sup>f</sup>	1.30±0.10	0.70 <sup>f</sup>	0.10 <sup>f</sup>
50	0.012±0.001	4.25±0.10	13±0.5	0.15 <sup>f</sup>	1.00±0.10	0.70 <sup>f</sup>	0.10 <sup>f</sup>
75	0.011±0.001	4.22±0.02	13±1	0.15 <sup>f</sup>	1.00±0.10	0.70 <sup>f</sup>	0.10 <sup>f</sup>
100	0.009±0.001	4.20±0.05	15±1	0.15 <sup>f</sup>	0.80±0.20	0.60 <sup>f</sup>	0.10 <sup>f</sup>
125	0.010±0.001	4.22±0.02	16±1	0.15 <sup>f</sup>	0.80±0.10	0.70 <sup>f</sup>	0.10 <sup>f</sup>
150	0.010±0.001	4.25±0.02	16±0.5	0.15 <sup>f</sup>	0.75±0.05	0.70 <sup>f</sup>	0.10 <sup>f</sup>
175	0.008±0.002	4.35±0.05	15.8±0.3	0.15 <sup>f</sup>	0.70±0.10	0.70	0.10 <sup>f</sup>
200	0.003±0.001	4.40±0.05	15±1	0.15 <sup>f</sup>	0.60±0.10	0.70 <sup>f</sup>	0.10 <sup>f</sup>
225	0.003±0.000	4.37±0.02	20.6±0.2	0.00 f			0.23±0.02
250	0.004±0.001	4.00±0.10	22±2	0.00 <sup>f</sup>			0.20±0.03

# Table S3. Fit parameters for the pressure scan at 31 $^{\circ}\mathrm{C}$

<i>p</i> [MPa ]	$I_{\mathrm{P},0}[\mathrm{a.u}]$	т	$I_0 \times 10^3$ [a.u]	σ	$I_{\mathrm{OZ},0}$ [a.u]	ζ [nm]	I <sub>bkg</sub> [a.u]
10	0.015±0.001	3.95±0.02	15±0.5	$0.00^{f}$			0.10±0.05
25	0.025±0.001	3.82±0.02	19±1	$0.00^{\mathrm{f}}$			0.10 <sup>f</sup>
50	0.032±0.001	3.68±0.03	23±1	$0.00^{\mathrm{f}}$	0.50±0.05	$0.80^{\mathrm{f}}$	$0.10^{\rm f}$
75	0.058±0.001	3.36±0.02	23±1	$0.00^{\mathrm{f}}$	1.00±0.10	$0.80^{\mathrm{f}}$	$0.10^{\rm f}$
100	0.050±0.001	3.35±0.03	30±1	$0.00^{\mathrm{f}}$	0.90±0.10	0.75 <sup>f</sup>	0.10 <sup>f</sup>
125	0.055±0.001	3.22±0.02	29.5±0.5	$0.00^{\mathrm{f}}$	0.90±0.10	$0.80^{ m f}$	0.10 <sup>f</sup>
150	0.055±0.003	3.15±0.05	30±2	$0.00^{\mathrm{f}}$	0.75±0.05	$0.80^{ m f}$	0.10 <sup>f</sup>
175	0.060±0.005	3.00±0.10	29±2	$0.00^{\mathrm{f}}$	0.80±0.01	$0.80^{ m f}$	0.10 <sup>f</sup>
200	0.060±0.003	2.90±0.05	30±1	$0.00^{\mathrm{f}}$	0.70±0.01	$0.80^{ m f}$	0.10 <sup>f</sup>
225	0.059±0.001	2.82±0.02	33±2	$0.00^{\rm f}$	0.50±0.10	$0.80^{ m f}$	0.10 <sup>f</sup>
250	0.057±0.002	2.73±0.03	32±0.5	$0.00^{\rm f}$	0.50±0.10	0.80±0.10	0.10 <sup>f</sup>

Table S4. Fit parameters for the pressure scan at 36  $^{\circ}\mathrm{C}$ 

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