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Conformation of oligo(ethylene glycol) grafted poly(norbornene) in solutions: A small angle neutron scattering study

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ABSTRACT

The conformation of newly synthesized amphiphilic poly(methoxyoligo(ethylene oxide) norbornenyl esters) macro-homopolymers in dilute solutions of toluene-d8 and D_2O was investigated by small angle neutron scattering (SANS). The macro-homopolymers consist of a polynorbornene (PNB) backbone with a degree of polymerization (DP) of 50, and each repeat unit has a grafted ethylene glycol (EG) side chain with an average DP of 6.6. The hydrophobic backbone and hydrophilic side chains interact differently with solvents of different polarity, which makes the polymer conformation very sensitive to the solvent quality. It was found that in a 0.5 wt.% toluene solution the polymers assume coil-like conformation and gradually contract and become more compact with increasing polymer concentration. In D_2O, the conformation of the polymers were studied at different concentrations: 0.1, 0.5, 1.0 and 2.0 wt.% and at different temperatures: 25, 44, 60 and 74 °C. The polymers are partially contracted in D_2O and their shape can be described by the form factor of a rigid cylinder. The second virial coefficient A_2 was extracted at three temperatures (25, 44 and 60 °C) and the theta point was estimated to be reached at ~45 °C. The attractive interactions between the polymers in D_2O increase with temperature, which leads to the polymer–solvent phase separation at the cloud point temperature (CPT). The polymer conformation remains virtually temperature independent below the CPT and at 74 °C polymers collapse and form compact structures with water soluble side chains in the shell.

1. Introduction

Oligo(ethylene glycol) (OEG) grafted comb-like polymers are of special fundamental and practical interest due to their versatile architecture and the unique properties of EG [1–8]. The OEG segments have been grafted to hydrophilic polymers such as poly(vinyl ether) [1] and poly(methacrylic acid) (PMAA) [2] as well as hydrophobic polymers such as polymethacrylate (PMA) [4–8] and polystyrene (PS) [3]. OEG-grafted polymers are promising materials in many fields such as in solid phase ionic conductors [9] and in modifying surfaces to prevent nonspecific protein or bacteria adhesion [10], etc. The structural properties of these polymers may be dramatically altered by small variation of external parameters such as temperature, pH, and concentration. As a result, they have been recently proposed as an alternative to poly(*N*-isopropylacrylamide) (PNIPAM) in many fields such as drug delivery [5]. These polymers phase separate as the temperature is raised (a lower critical solution temperature (LCST) system) and the cloud point temperature (CPT) can be controlled by varying the number of EG repeat units in the side chain.

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The information on the conformation of these polymers at different conditions, for example, temperature- or pH-induced coil-to-globule transition, is required before designing their applications. The conformation of the macro-homopolymers with both loosely [11–14] and densely [15–16] grafted EG side chains have been investigated. In a light scattering study of a dilute solution of PNIPAM grafted with ~7 wt.% PEG chains, a single chain spherical core-shell nanostructures were observed in which the collapsed PNIPAM backbone formed the core at temperatures above the LCST [11]. In concentrated solutions, the formation of spherical aggregates consisting of a few polymer chains was detected [12,17]. Previous computer simulation studies of loosely grafted amphiphilic comb-like polymers in selective solvents focused on the kinetics of the coil-to-globule transition and showed that after reaching the equilibrium the formed globules were coated with solvophilic segments [13–14]. A multi-angle light scattering study of comb-like polymers consisting of a PS main chain (M_w: 10^4–10^8 g/mol) with poly(ethylene glycol) side chains (DP = 50) attached to each styrene repeat unit concluded that the structure of polymers in aqueous solutions were consistent with a worm-like chain model with a persistence length of 168 Å [15]. A Transmission Electron Microscopy investigation of the chain conformation of OEG-grafted PMMA confined at the polymer/water interface demonstrated that the radius of gyration R_g scaled with the number of the backbone segments (N) as $R_g \sim N^{0.69\pm0.02}$ [16].

Recently, the different hydration behaviors of the carbonyl groups and the ether groups on the side chain of poly(2-(2-methoxyethoxye)ethyl methacrylate) (PMEO$_2$MA) polymers in water were revealed by infrared spectroscopy [7]. The results suggested that the hydrogen bonding between water molecules and the carbonyl group was thermodynamically more stable than that of the ether group and large parts of them would be retained at the temperature above the phase transition temperature. The study also indicated that the steric hindrance affected the formation of hydrogen bonding between water molecules and functional groups on the side chain. Using ^{1}H NMR, dynamic light scattering and turbidimetry, the phase transition of copolymers of MEO$_2$MA and OEGMA in water were investigated, and it was found these copolymers exhibited a sharp and reversible LCST, accompanied by the coil-to-globule transition [5].

SANS is a powerful technique to study the solution properties of polymers on length scales on the order of 10–1000 Å. In this paper we describe the results of the SANS studies of the conformation of our newly synthesized OEG-grafted polynorbornene (PNB) in two different solvents: D$_2$O and toluene-d8, which exhibit significantly different solvent quality with respect to the backbone and side chain polymers. Solvent quality is expected to affect the conformation of comb-like polymers with a hydrophobic backbone and hydrophilic side chains more significantly than the conformation of the polymers with similar backbone and side chain hydrophobicity. The solvent quality of aqueous solutions is further altered by increasing the temperature. The studied polymers have polynorbornene backbone with the DP = 50 and each backbone repeat unit has a grafted EG side chain with the average DP = 6.6 [18].

2. Experimental section

2.1. Materials

The chemical structure of the macro-homopolymer is shown as an insert in Fig. 1. The polymers were made via ring-opening metathesis polymerization (ROMP) with Grubbs Catalysis [18]. The polymerization was terminated by injecting excess of vinyl ethyl ether. The degree of polymerization of the macro-homopolymer EG$_{6.6}$NB is 50. The polydispersity of the polymer is 1.2, determined by gel permeation chromatography. The polymers have a *cis*-vinyl content of 44 wt.% and *trans*-vinyl content of 56 wt.% as determined by NMR. The density of the backbone is assumed to be that of PNBE, i.e., 1.35 g/cm^3 and of the side chain is assumed to be that of PEG, 1.12 g/cm^3.

2.2. SANS measurements

SANS measurements were performed at the National Institute for Standards and Technology Center for Neutron Research on the NG7 30 m instrument with a neutron wavelength of $\lambda = 6.0$ Å ($\Delta\lambda/\lambda \approx 0.15$). Two sample-detector distances were used (1.50 m and 13.0 m with a 25 cm offset), which leads to an overall q-range of $0.0042\ \text{Å}^{-1} < q = 4\pi\lambda^{-1}\ \sin\theta < 0.40\ \text{Å}^{-1}$, where 2θ is the scattering angle. The data were corrected for instrumental background as well as detector efficiency and put on absolute scale [cross-section $I(q)$ in units of cm^{-1}] based on the direct beam flux method. Scattering from the solvent was subsequently subtracted in proportion to its volume fraction. The neutron cross-section for dilute solutions is described by Zimm expression [19]:

$$I(q) = \frac{c}{K}\frac{P(q)}{1 + 2cA_2M_WP(q)} \tag{1}$$

where $P(q)$ is the form factor, c is the concentration in g/ml, $K = (N_A\ \rho^2)/(M_W\Delta\rho^2)$, M_W is the weight − average molecular weight, $\Delta\rho$ is the scattering length density difference between the polymers and solvent, ρ is the mass density of a polymer and A_2 is the second virial coefficient which characterize the average interactions between two polymers in infinite dilute limit.

The A_2 may be extracted from the plot of $c/I(0)$ as a function of c via [20]:

$$\frac{c}{I(q=0)} = K(1 + 2A_2cM_W) \tag{2}$$

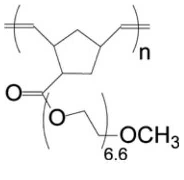

Fig. 1. The chemical structure of the macro-homopolymer EG$_{6.6}$NB.

The scattering length density of the PNB (7.9×10^{-7} Å^{-2}) and the EG (6.2×10^{-7} Å^{-2}) are similar and therefore SANS detects the global conformation of the polymer.

The temperature range covered in the experiments was 25–74 °C and the temperature was controlled to better than ±0.2 °C using a water circulation bath. Before starting the measurements, solutions were equilibrated at each temperature for 60 min. The run times at each temperature at the 13.0 m sample-detector distance (SDD) were 30 min. At SDD = 1.5 m, the run time was 5 min.

3. Results and discussion

3.1. Conformation of the $EG_{6.6}NB$ macro-homopolymer in toluene-d8

Toluene is a good solvent for PNB homopolymers [21]. Therefore, the conformation of the $EG_{6.6}NB$ polymers in toluene is determined by the repulsive interactions between PNB repeat units and the solvent-mediated interactions between EG side chains, which could be either repulsive or attractive depending on the solvent quality for EG side chains. The $EG_{6.6}NB$ polymers studied in this work were dissolved in toluene and D_2O at room temperature. Visual observations revealed that the solution remains optically transparent and no precipitant was formed. The solutions remain clear up to their cloud point temperature (CPT). The CPTs are 63, 64, 65 and 68 °C for 2.0, 1.0, 0.5 and 0.1 wt.% solutions, respectively.

The SANS data taken from 0.5, 1.0 and 2.0 wt.% solutions of $EG_{6.6}NB$ in toluene at 25 °C are shown in Fig. 2a. An upturn at low q with the slope of -2 is due to the scattering from polymer clusters and is observed for all three solutions. Following the low q upturn, a plateau is clearly observed over a wide q range, which indicates that clusters have a minor influence on the scattering in the higher q regime and only a small fraction of the polymers belongs to the clusters. Except the low q upturn, the scattering may be therefore attributed to polymers molecularly dispersed in dilute solutions. The Debye function which describes the form factor of a random coil was used to fit the data and the fits are shown as solid lines on the curves. It was found that the radius of gyration of the polymers in the 0.5, 1.0 and 2.0 wt.% solutions is $R_g = 55 \pm 1$, 53 ± 1 and 45 ± 1 Å, respectively. Extrapolating the values of the R_g to zero concentration, one obtains the R_g $(c = 0) = 60 \pm 3$ Å. The overlap concentration for this polymer in toluene is estimated to be $c^* = M_W/N_A \ V \sim 4.9$ wt.%, where $V = 4\pi R_g^3/3$, N_A is the Avogadro number and $R_g = 60$ Å. The deviation from the Debye function is observed at the length scales of 30–40 Å, which correspond to $q = 0.15$–0.20 Å^{-1}. The reason of it becomes clear when the data are presented in the form of the Kratky plot, $I(q) \times q^2$ as a function of q (see Fig. 2b). The coil behavior is observed for the polymers in 0.5 wt.% solution over a wide q range and the plateau evolves into a hump with increasing polymer concentration. It is most pronounced for the 2.0 wt.% solution. The hump is often observed in scattering patterns from star-like polymers when the data are represented in the form of the Kratky plot [22]. The observed effect suggests that individual polymers are contracting and becoming more compact, which is consistent with the decrease of the overall size of the polymers with concentration. At $q > 0.2$ Å^{-1}, $I(q) \times q^2$ linearly increases with q, which indicates a transition to the rod-like behavior of the polymer chain on a local scale [23]. The rod-like structure is observed on the length scales of 30–40 Å, which is similar to the behavior of PNB macro-homopolymers in a theta solvent CS_2 where this transition starts at 40 Å [21]. This observation suggests that short EG side chains do not extend the PNB backbone significantly, as one might have expected.

3.2. Conformation of the $EG_{6.6}NB$ macro-homopolymer in D_2O

The solution properties of PEG (or Poly ethylene oxide (PEO)) in water have been investigated extensively. Although PEG molecules often forms clusters in water, the origin of the chain aggregation has not been completely understood [24–25], water has been reported to

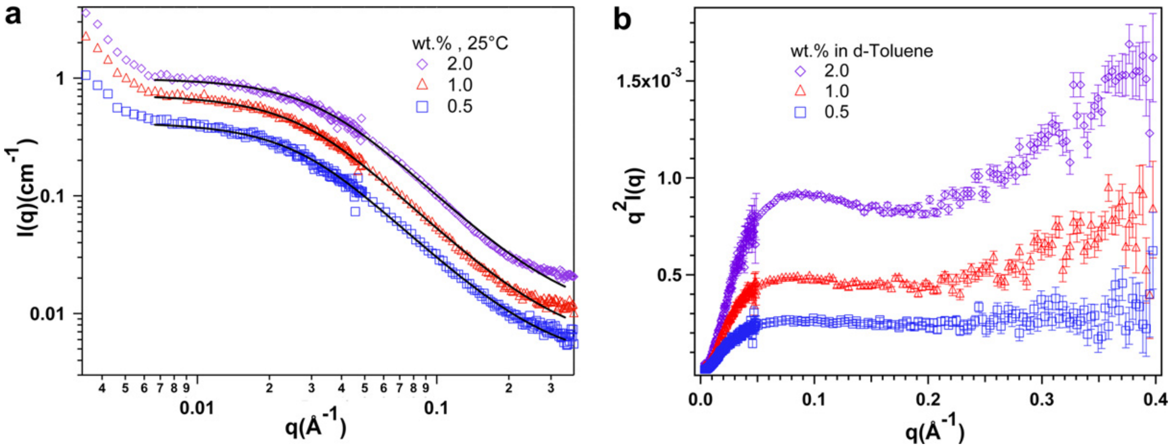

Fig. 2. (a) SANS curves of the $(EG_{6.6}NB)_{50}$ macro-homopolymer in toluene-d8. (b) The Kratky plot of the data shown in Fig. 1a. The solid line on the data of the polymers in toluene is a fit to the form factor of the Debye function. The error bars on the SANS curves in Fig. 1a are not added for the sake of clarity.

be a good solvent for PEG macro-homopolymers based on the measurements of the second virial coefficient A_2 and the swelling exponent [26–27]. At the same time, water is a non-solvent for the PNB backbone and thus the polymers can be dissolved in water only if a sufficient amount of the hydrophilic EG side chains are available. If the EG side chains are long enough, excluded volume interactions between EG side chains may completely screen out the attractive interactions between PNB repeat units and the polymers expand. For shorter EG side chains, the hydrophilic interactions weaken, the attractive interactions between PNB repeat units become more important, and the polymers contract. Below a certain limiting DP, one eventually approaches the solubility limit and formation of compact globules coated with EG chains may be anticipated.

The conformation of the $EG_{6.6}NB$ macro-homopolymer in D_2O was studied as a function of the solution concentration as well as temperature. Fig. 3 presents the SANS data of the polymers in solutions of different concentrations at 25, 44, 60 and 74 °C. A low-q upturn, signifying the presence of polymer clusters is seen for all concentrations except for the 0.1 wt.% solution. The scattering intensity increases with temperature due to increasing attractive interactions between polymers, which are expected to cause polymer–solvent phase separation at the CPT [28].

The second virial coefficient A_2 has been used to describe the interparticle and intermolecular interactions in various systems such as dilute solutions of fullerenes [20], proteins [29], and catalysts [30], in addition to synthetic polymers [19,26,31–32]. In some cases, the solutions were not homogeneous and a small fraction of clusters was observed [19,30], which is similar to results reported in this study. In a recent SANS investigation of the PEG aqueous solutions, Zimm equation (Eq. (1)) was used to fit the SANS data at different temperatures and the interaction parameter A_2 was extracted as a fitting parameter [19]. At temperatures below the theta temperature, the values of A_2 were positive, indicating repulsive intermolecular interactions between PEG molecules in D_2O. The values of A_2 decreased with temperature and became negative above the theta temperature.

In this study, the value of the A_2 was extracted from Eq. (2) by plotting the data as $c/I(0)$ vs. c. The values of $I(0)$ were obtained by extrapolating the data at low q ignoring scattering from clusters at different temperatures (see Fig. 4). The second virial coefficient of the polymers in D_2O at 25, 44 and 60 °C is $A_2 = (6.3 \pm 1.1)10^{-4}$ mol cm^3 g^{-2},

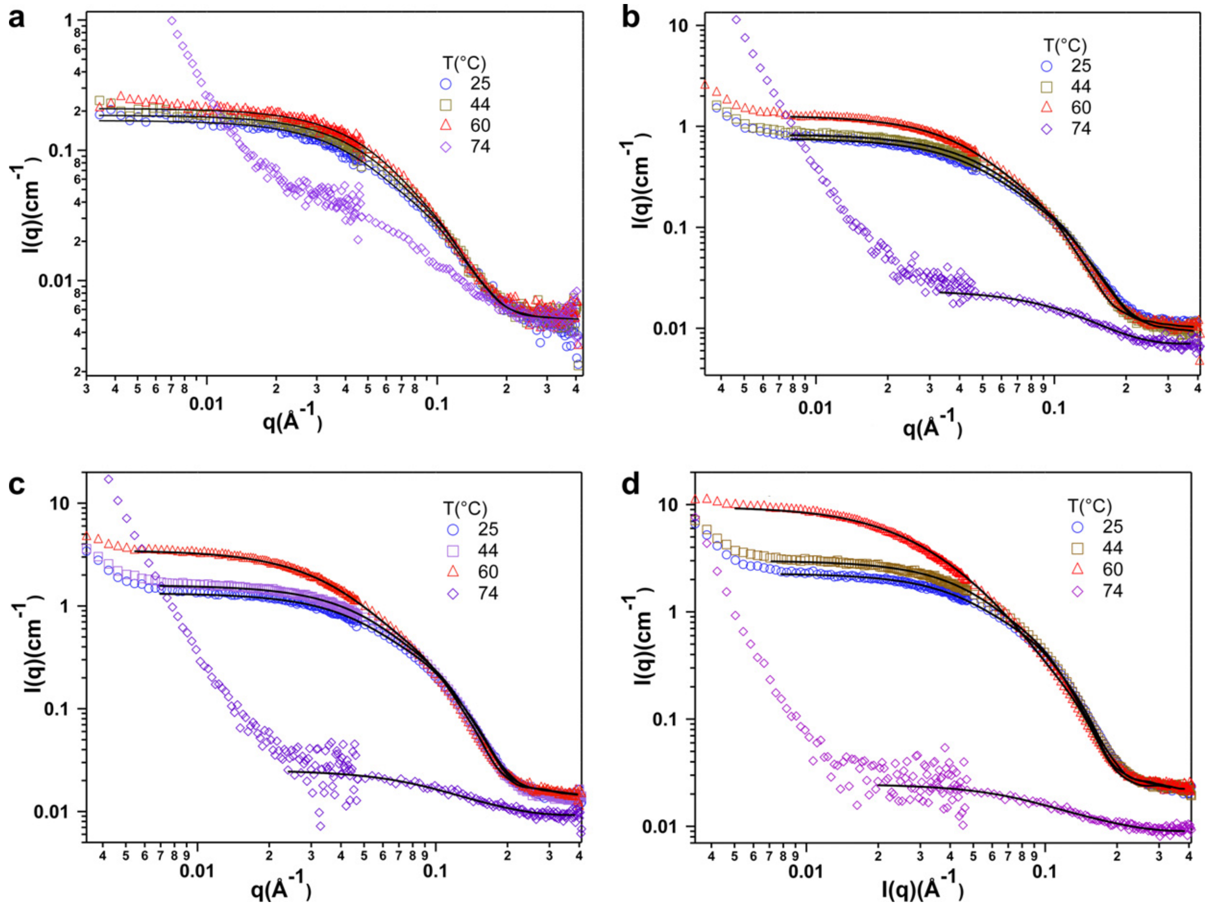

Fig. 3. SANS data of the $(EG_{6.6}NB)_{50}$ macro-homopolymers in D_2O at (a) 0.1; (b) 0.5; (c) 1.0 and (d) 2.0 wt.% and different temperatures. The solid line on the data at 25, 44 and 60 °C is a fit to Eq. (1) as shown in the text. The solid line on the data at 75 °C is a fit to the form factor of an ellipsoid. The error bars on the SANS curves are not added for the sake of clarity.

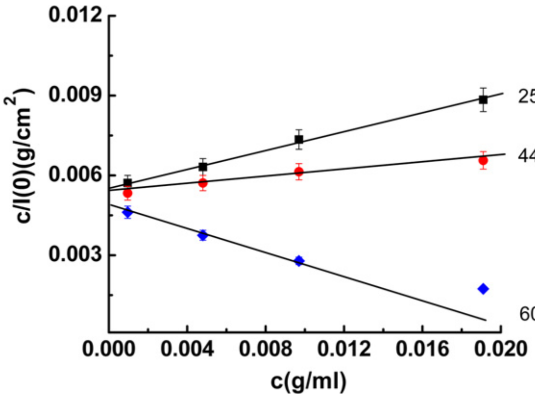

Fig. 4. Virial plot for the concentration series of the polymers in D_2O at three different temperatures.

$A_2 = (2.5 \pm 0.8)10^{-4}$ mol cm^3 g^{-2} and $A_2 = -(8.6 \pm 1.3)10^{-4}$ mol cm^3 g^{-2}, respectively. In comparison, the A_2 of the polymers in toluene at 25 °C is $(16.3 \pm 1.5)10^{-4}$ mol cm^3 g^{-2}. The values of the A_2 at different temperatures indicate that the attractive interactions increase with temperature due to deteriorating solvent quality of water as well as stronger hydrophobic interactions between the PNB backbones. The theta temperature, at which the $A_2 = 0$, of this polymer in D_2O was estimated to be close to 45 °C.

The SANS data (see Fig. 3) were analyzed using Eq. (1) in which $P(q)$ was chosen to be a form factor of a rigid cylinder with a polydisperse cross-section radius. The value of the A_2 was fixed during the fitting procedure at each temperature. A polydispersity of 0.15–0.2 was found to best describe the data. The solid lines in Fig. 3 are the fits to Eq. (1) at each temperature. The cylinder parameters thus obtained are listed in Table 1 which demonstrates minor effect of the concentration and temperature (and thus intermolecular interactions) on the polymer conformation in the studied range of parameters, except probably 2.0 wt.% solution at 60 °C. It may also be seen in Fig. 4, where the point corresponding to the 2.0 wt.% solution at 60 °C deviates strongly from the linear fit to the first three points at smaller concentrations. The observed deviation may be caused uncertainties in the sample preparation and thus only data for $c < 0.012$ g/ml were used for determining the second virial coefficient at $T = 60$ °C.

Table 1
Results from the modeling of the SANS data

25 °C			44 °C			60 °C		
C (wt.%)	*R* (Å)	*L* (Å)	*C* (wt.%)	*R* (Å)	*L* (Å)	*C* (wt.%)	*R* (Å)	*L* (Å)
0.1	15	113 ± 1	0.1	16	102 ± 1	0.1	16	98 ± 1
0.5	15	113 ± 3	0.5	17	97 ± 3	0.5	17	104 ± 3
1.0	15	116 ± 4	1.0	16	106 ± 3	1.0	16	113 ± 6
2.0	16	118 ± 6	2.0	16	119 ± 6	2.0	16	92 ± 17

In Table 1, *C* is the solution concentration in wt.%; *R* is the cross-section radius of a cylinder and it has a polydispersity of 0.15–0.2; *L* is the length of a cylinder.
The errors of the length *L* were determined by the uncertainties of the values of A_2.

Assuming that the length of the norborneyl repeat unit is 5 Å [21], the contour length of fully extended PNB backbone is expected to be 50 × 5 = 250 Å which leads to a conclusion that the PNB backbone is partially collapsed in aqueous solutions. As soon as the overall polymer conformation in D_2O is defined by a balance between attractive interactions between the PNB backbone repeat units and the excluded volume interactions between EG side chains, the observed contraction indicates that the length of the side chains of the studied polymers is not sufficient to effectively screen out the interactions between PNB repeat units.

Above the CPT, the solution phase separates and polymer starts to precipitate, which results in a decreased scattering intensity. The observed upturn at $q < 0.015$ Å^{-1} at 74 °C may be attributed to scattering from large aggregates still present in solution, while the scattering at higher q values may be attributed to the scattering from the dissolved individual polymers. The very small value of the intensity at q around 0.2–0.4 Å^{-1} suggests that only about a few percent of the polymers initially dissolved in water at 25 °C remain in solution at 75 °C and most of the polymers exist in the form of aggregates. The solid lines in Fig. 3 at 75 °C are fits to a form factor of ellipsoid and the values of fitting parameters are: the radius of the rotation axis $R_a = 27 \pm 1$ and $R_b = 12 \pm 1$; $R_a = 33 \pm 10$ and $R_b = 11 \pm 2$; $R_a = 36 \pm 10$ and $R_b = 10 \pm 4$ Å for 0.5, 1.0 and 2.0 wt.% solutions, respectively. The large errors of the sizes of the ellipsoids obtained from the fitting are due to relatively low statistics of the data. The data of obtained for the 0.1 wt.% solution were not fitted because of the strong contribution of the scattering from the aggregates. Based on results of computer simulation [13–14,33] and experimental [11] studies it is reasonable to assume that the collapsed polymers have a core-shell structure with the water soluble EG side chains in the shell.

4. Summary

Our results demonstrate that the conformation of studied OEG-grafted PNB polymer solutions is controlled by interactions between the backbone, side chain and the solvent molecules. In *d*-toluene the global conformation of the backbone PNB polymer is not perturbed significantly by the presence of short EG side chains and is described by the form factor of random-coil on length scales longer than 40 Å in 0.5 wt.% solution. The polymers contract with increasing concentration and the conformation of polymers starts to deviate from the random-coil behavior. Water is a selective solvent for the OEG side chains and the global polymer conformation in this solvent is determined by the balance between excluded volume interaction of side chains and attractive interactions between unsoluble PNB repeat units. The chains are partially contracted already at 25 °C (i.e. far away from the cloud point) and the global conformation at this temperature is close to cylindrical. The second virial coefficient (A_2) was used to characterize the interactions between polymers in aqueous solutions at different temperatures and the estimated theta temperature was found to be close to 45 °C. By fitting the SANS data to the Zimm equation, the dimension of the polymers were extracted. The size of individual polymers remains the cloud point temperature. At 74 °C, most of the polymers precipitate and the remaining in the solution few percent of the individual polymers collapse to form compact ellipsoids.

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