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Dependence of nanophase separated structure of epoxy hydrogels on swelling conditions investigated by SANS

Noemi Szekély [a], Ivan Krakovský [b,*]

[a] KFKI Research Institute for Solid State Physics and Optics, P.O. Box 49, Budapest H-1525, Hungary
[b] Department of Macromolecular Physics, Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, 180 00 Prague 8, Czech Republic

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ABSTRACT

A hydrophilic non-stoichiometric epoxy network was prepared by end-linking reaction of α,ω-diamino terminated poly(oxypropylene)-*b*-poly(oxyethylene)-*b*-poly(oxypropylene) (POP–POE–POP) and diglycidyl ether of Bisphenol A propoxylate (PDGEBA) at the excess of amino groups. Series of epoxy hydrogels swollen to various degrees was prepared by swelling of the epoxy network in D_2O and solutions of inorganic salt (KNO_3) in D_2O, respectively, and investigated by small-angle neutron scattering (SANS). Degree of swelling was controlled in two ways: by partial evaporation of the solvent and by KNO_3 concentration in the swelling solution. Nanophase separated structure of all hydrogels was confirmed by SANS. Scattering data were fitted to the Teubner–Strey model assuming bicontinuous locally lamellar structure of the hydrogels. Changes in SANS profiles induced by the presence of KNO_3 in swelling solutions reflect a refinement of the nanophase separated structure of hydrogels caused by improvement of POE–D_2O interaction by means of breakage of deuterium-bonded structure of D_2O by nitrate anions.

1. Introduction

Epoxy resins represent an important class of industrial polymers because of their excellent mechanical, thermal and dielectric properties. They are widely used in many technical applications such as surface coatings, structural adhesives and composites in electronic or aerospace industries [1].

In preparation of epoxy resins reaction of diamino-functionalized prepolymer with a diepoxide, e.g., α,ω-diamino terminated polyoxypropylene (POP) with diglycidyl ether of Bisphenol A (DGEBA) is usually used. During the reaction, the initially liquid reaction mixture passes through a gel-point and solidifies into the polymer network. When hydrophobic POP is substituted with hydrophilic polyoxyethylene (POE) hydrophilic epoxy networks can be prepared. Hydrophilic epoxy networks possess properties that can be very attractive for applications in biomedicine.

In our previous paper [2], we have reported results of investigation of epoxy hydrogels obtained by swelling of hydrophilic epoxy networks prepared by reaction of diamino-functionalized POP–POE–POP copolymer with diglycidyl ether of Bisphenol A propoxylate (PDGEBA) in D_2O. Nanophase separated structure of all hydrogels consisting of water-rich and hydrophobic phases was revealed by small-angle neutron scattering (SANS). Experimental data were fitted to Teubner–Strey model [3] assuming bicontinuous locally lamellar structure of the hydrogels and dependence of the structure of hydrogels on the composition of the epoxy networks used in swelling was determined.

This paper explores the dependence of the structure of epoxy hydrogels on the degree of swelling. To this purpose, one of the hydrogels from the previous system (EP115, see Ref. [2]) was chosen and the degree of swelling was controlled in two ways: (a) by partial evaporation of the solvent (D_2O), and, (b) by concentration of inorganic salt (KNO_3) in the swelling solution. SANS was exploited in investigation of the structure of hydrogels and experimental data obtained were analysed again using Teubner–Strey

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* Corresponding author. Tel.: +420 221 912 747; fax: +420 221 912 350.
E-mail address: ivank@kmf.troja.mff.cuni.cz (I. Krakovský).

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model. Dependence of the structure of the hydrogels on the swelling conditions is discussed.

2. Experimental

2.1. Materials

In the preparation of the epoxy network α,ω-diamino terminated poly(oxypropylene)-*block*-poly(oxyethylene)-*block*-poly(oxypropylene) (Jeffamine® ED600, Huntsman) and diglycidyl ether of Bisphenol A propoxylate (PDGEBA, Fluka) were used. Molar mass of ED600 is ca. 600 g mol^{-1} and POE content is about 60 wt%. Before using, all reactives were dried at 40 °C for 48 h in a vacuum oven. Concentrations of amino groups in ED600 and epoxy groups in PDGEBA determined by titrations were $c_{NH_2} = 3.2 \times 10^{-3}$ mol g^{-1} and $c_E = 2.92 \times 10^{-3}$ mol g^{-1}, respectively.

The epoxy network (EP115, see Ref. [2]) was prepared at initial molar ratio of reactive groups, $r = 2[NH_2]_0/[E]_0$ equal to 1.50. $[NH_2]_0$, and $[E]_0$ are initial molar concentrations of amino and epoxy groups, respectively. Both components were first stirred at 100 °C for about 15 min and then poured into Teflon moulds. Curing reaction proceeded at 120 °C for 48 h in nitrogen atmosphere. The network prepared was transparent.

Extractable fraction (sol) remaining in the epoxy network was removed before swelling and SANS measurements. This was realized by triple extraction of the network in good solvent (toluene).

2.2. Measurements

2.2.1. Swelling

First, a few samples of the hydrogel fully swollen in D_2O (first sample in Table 1) were prepared by immersion of disc specimens cut from dry and extracted network in D_2O at 25 °C and its swelling to equilibrium. Samples of the hydrogels partially swollen in D_2O were prepared from the fully swollen samples by evaporation of the proper amount of D_2O in air and their equilibration by enwrapping in aluminium foil for 12 h. The rest of samples was prepared by equilibrium swelling of disc specimens cut from the dry and extracted network in the series of solutions of KNO_3 in D_2O at concentrations given in Table 1 at 25 °C. Volume fraction of water in hydrogels, v_{D_2O}, was calculated from the mass increase due to water adsorption assuming additivity of volumes as

$$v_{D_2O} = \frac{1}{1 + \left(\frac{m}{m_0} - 1\right)\frac{d_s}{d_0}}$$

where m, and m_0 are the masses of the hydrogel and dry extracted network, and d_s and d_0 are the specific masses of the swelling solution and dry extracted network, respectively. Volume fractions of other components in hydrogels (POE, POP and PDGEBA) given in Table 1 were also calculated on the assumption of volume additivity from the compositions of dry extracted networks determined spectroscopically.

Table 1
Composition of the systems investigated: v_{POE}, v_{POP}, v_{PDGEBA} and v_{D_2O}, denote the volume fractions of POE, POP, PDGEBA and D_2O, respectively.

Sample	v_{POE}	v_{POP}	v_{PDGEBA}	v_{D_2O}
EP115 + D_2O (fully swollen)	0.130	0.099	0.358	0.413
EP115 + D_2O (part. swollen)	0.148	0.113	0.407	0.332
EP115 + D_2O (part. swollen)	0.179	0.137	0.493	0.191
EP115 + 0.01 M KNO_3	0.153	0.117	0.421	0.309
EP115 + 0.02 M KNO_3	0.152	0.116	0.418	0.314
EP115 + 0.05 M KNO_3	0.154	0.118	0.426	0.302
EP115 + 0.10 M KNO_3	0.149	0.114	0.411	0.326

2.2.2. Small-angle neutron scattering

The SANS measurements were performed with the small-angle neutron scattering diffractometer "Yellow Submarine" operating on the cold neutron beam line at the Budapest Research Reactor [4]. A mean neutron wavelength $\lambda = 4.1$ Å, and sample-detector distances 1.3 and 4 m were used, covering the range of the magnitudes of scattering vector $q = 0.01–0.36$ Å^{-1}, data influenced by the proximity of beam-stop (0.01–0.02 Å^{-1}) were excluded from the analysis. The samples were thermostated at 25.0 ± 0.1 °C. Immediately before the measurements, hydrogel samples were closed between two quartz windows separated by a sealing from silicone rubber and mounted into aluminium holders. The scattering intensities were radially averaged and corrected for the sample transmission, room background and detector efficiency using standard procedures.

3. Results and discussion

SANS profiles obtained on the hydrogels prepared by swelling in D_2O are shown in Fig. 1. All the samples exhibit a distinct scattering peak with height increasing with increasing degree of swelling expressed by the volume fraction of water, v_{D_2O}. Position of the scattering peak, q_{max}, shifts to high q-region and, consequently, Bragg distance,

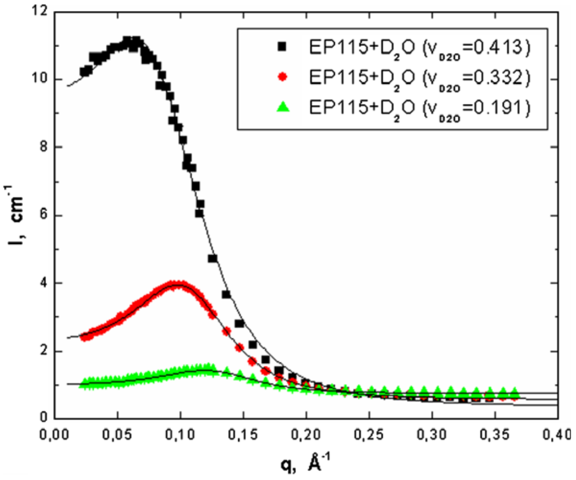

Fig. 1. SANS scattering profiles (scattering intensity I vs. magnitude of scattering vector q) obtained from the partially swollen epoxy network in D_2O at 25 °C. Solid lines represent fits according to Teubner–Strey model.

D_B, defined by $D_B = 2\pi/q_{max}$, drops with decreasing swelling, obtaining the value ca. 108 Å for the fully swollen sample in which $v_{D_2O} = 0.41$ and 55 Å for the sample with $v_{D_2O} = 0.19$, respectively (see Table 2).

SANS profiles obtained from the hydrogels prepared using solutions of KNO_3 in D_2O at the concentrations given in Table 1 are shown in Fig. 2. Presence of KNO_3 in the swelling solution causes a substantial drop of scattering intensity in low q-region. Interestingly, swelling of the network EP115 in KNO_3 solutions at the concentrations used provides hydrogels with a very similar content of water (see Table 1) which is also confirmed by a very close levels of incoherent scattering background in high q-region. However, the profiles differ again mainly in low q-region: with increasing KNO_3 concentration the position of scattering peak shifts to higher q-values. The values of the Bragg distance calculated from the peak positions change from 66 Å in 0.01 M KNO_3 to 58 Å in 0.1 M KNO_3 solution, respectively. The former value equals to the value determined for the sample partially swollen in D_2O to similar degree (see Table 2 and Fig. 1), however, the scattering intensities in low q-region are somewhat smaller for the sample swollen in D_2O. Therefore, it can be concluded that despite the amount of water in the hydrogels swollen in KNO_3 solutions is almost the same the distribution of water molecules is different and depends on the concentration of inorganic salt.

Analysis of the SANS profiles in descending region of scattering intensity shows that coherent scattering intensity (i.e., the part of scattering intensity obtained by subtraction of the constant background attributed to incoherent scattering) decays for all samples as q^{-n} with $n \approx 4$. Only for the sample fully swollen in D_2O somewhat steeper decay corresponding to $n \approx 4.4$ was determined. These values are much higher than value expected for the polymer networks swollen in good solvent ($n \leqslant 2$) where it reflects the fluctuations of the hydrogel composition and density due to the thermal movement of the polymer segments and solvent molecules [5–10]. Since the neutron scattering properties of D_2O differ significantly from the other components present in hydrogels (see Table 3), a kind of phase separated structure with domains rich and poor in D_2O is expected. Because the length scale of the phase separation as indicated by the values of the Bragg distance given above is of the order of nanometers it is the case of nanophase separation. Moreover, the nanophase structure of the hydrogels has to be bicontinuous because space connectivity of the epoxy network has to be conserved in the swollen state and water-rich domains have to be also interconnected.

Table 2
SANS parameters obtained for epoxy hydrogels: position of the scattering peak, q_{max}, Bragg's distance, $D_B = 2\pi/q_{max}$, values of the scattering invariant determined experimentally, Q (exp.).

Sample	q_{max} (Å^{-1})	D_B (Å)	Q (exp.) 10^{20} (cm^{-4})
EP115 + D_2O (fully swollen)	0.058	108	105
EP115 + D_2O (part. swollen)	0.095	66	57
EP115 + D_2O (part. swollen)	0.115	55	24
EP115 + 0.01 M KNO_3	0.095	66	75
EP115 + 0.02 M KNO_3	0.102	62	75
EP115 + 0.05 M KNO_3	0.102	62	70
EP115 + 0.10 M KNO_3	0.109	58	59

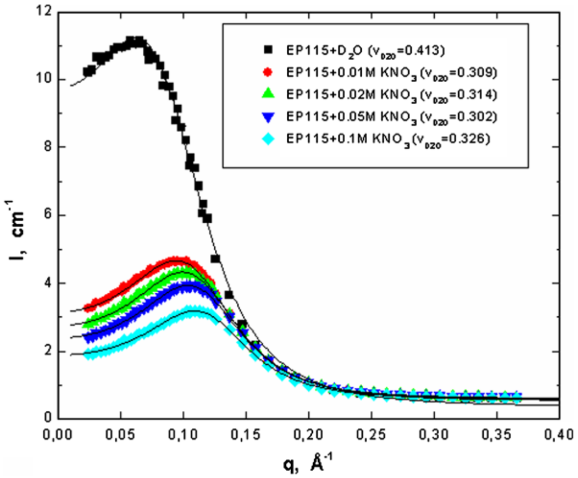

Fig. 2. SANS scattering profiles obtained from the epoxy network swollen in KNO_3 solutions in D_2O at 25 °C. Solid lines represent fits according to Teubner–Strey model.

Table 3
Specific masses, d, and neutron scattering length densities, ρ, of the components at 25 °C.

Compound	d (g cm^{-3})	ρ 10^{10} (cm^{-4})
POE	1.08	0.61
POP	1.01	0.35
PDGEBA	1.09	1.15
D_2O	1.10	6.34

To confirm these ideas, values of the scattering invariant, Q, were calculated by numerical integration of the experimental SANS profiles from which constant incoherent background, I_B, was subtracted (see Table 2) as $Q = \int_0^\infty q^2[I(q) - I_B]dq$. Scattering intensities out of the measured range ($q > 0.37$ Å^{-1}) needed in the integration were approximated by extrapolation of experimental scattering profiles by q^{-4} decay. Polychromacity of the primary neutron beam (ratio of standard deviation to mean value of wavelength $\Delta\lambda/\lambda = 0.08$, [4]) was also taken into account in the calculation according to formula given in Ref. [11].

The experimental values of the scattering invariant can be compared with values expected from a proper two-density model of the nanophase separated structure of the system:

$$Q = 2\pi^2 v_A v_B (\rho_A - \rho_B)^2 \tag{1}$$

where v_A, v_B and ρ_A, ρ_B are the volume fractions and neutron scattering length densities of phases, respectively. Sharp interface between phases is assumed, however, no assumption about the morphology of the system is needed.

In Tables 4 and 5, the values of the scattering invariant calculated for two hypothetical models which differ in compositions of the hydrogel phases are given. In the model I, it is assumed that the two phases consist of D_2O and organic components (POE, POP and PDGEBA), respectively.

Table 4

Parameters calculated assuming two-phase model structure (model I): phase A = $D_2O(+KNO_3)$, phase B = POE + POP + PDGEBA. v_A, v_B and ρ_A, ρ_B denote the volume fractions and neutron scattering length densities of phases, $\langle(\Delta\rho)^2\rangle$ is the mean square density fluctuation of the scattering length density, and Q is the scattering invariant calculated by $Q = 2\pi^2\langle(\Delta\rho)^2\rangle$.

Sample	v_A	v_B	$\lvert\rho_A - \rho_B\rvert$ 10^{10} (cm^{-2})	$\langle(\Delta\rho)^2\rangle$ 10^{20} (cm^{-4})	Q 10^{20} (cm^{-4})
EP115 + D_2O (fully swollen)	0.413	0.587	5.44	7.19	141.9
EP115 + D_2O (part. swollen)	0.332	0.668	5.44	6.58	129.8
EP115 + D_2O (part. swollen)	0.192	0.808	5.44	4.59	90.6
EP115 + 0.01 M KNO_3	0.310	0.690	5.44	6.34	125.2
EP115 + 0.02 M KNO_3	0.315	0.685	5.44	6.40	126.3
EP115 + 0.05 M KNO_3	0.302	0.698	5.44	6.25	123.4
EP115 + 0.10 M KNO_3	0.326	0.674	5.44	6.52	128.6

In the model II, the phases consist of mixture of hydrophilic component (POE) with D_2O and mixture of hydrophobic components (POP and PDGEBA), respectively. Volume fractions of the phases in the models (see Tables 4 and 5) were calculated using data given in Table 1 and assuming additivity of volumes. Neutron scattering length densities of phases in the models were estimated as volume averages of their constituents[1]. Values of the specific mass, d, and neutron scattering length densities of the constituents, ρ, at 25 °C are given in Table 3. The densities and neutron scattering length densities of the KNO_3 solutions of the concentrations used ($c_{KNO_3} \leq 0.1$ M) differ less than 1% and they were approximated by the values for D_2O.

For the sample fully swollen in D_2O, the value of Q lies between the values predicted by the above two models, being somewhat closer to the model II. In other words, not all POE chains are mixed with D_2O in the water-rich phase, but a part of POE is also in the other phase.

For the samples partially swollen in D_2O, within limits of experimental accuracy, the experimental values of Q are close to the values calculated for the model II. Therefore, partial drying of the sample swollen in D_2O leads to a release of POE from the hydrophobic phase and its transfer to the water-rich phase.

The same is valid for the samples swollen in KNO_3 solutions, the experimental values of Q decrease with increasing KNO_3 concentration in the swelling solution[2], being closer to the values calculated for the model II. Since the swelling degree almost do not change in this series, the decrease in Q is not possible without the change of the composition and volume occupied by individual phases. Similar to the samples partially swollen in D_2O, increasing amount of KNO_3 in the swelling solution leads to a growing release of POE from the hydrophobic phase and its transfer into the water-rich phase. We think that namely this transfer of POE is responsible for the drop of the scattering intensity in low q-region shown in Fig. 2.

So far, in the discussion of the experimental data the values of the scattering invariant were used, no assumptions about possible geometrical form of the hydrogel phases in the above models were made. Now, full information contained in scattering profiles will be used to obtain more information about the structure of hydrogels. To this purpose, experimental data has to be fitted to a proper model. Since the structure has to be bicontinuous (see above), we used Teubner–Strey model [3] in which the structure of system is supposed to be locally lamellar, i.e., it can be described by two structural parameters (characteristic lengths): periodicity, D, and persistence length of the lamellar order, ζ.

Teubner–Strey formula for scattering intensity (per unit irradiated volume) from this system reads

$$I(q) = \frac{8\pi\langle(\Delta\rho)^2\rangle}{\zeta} \cdot \frac{1}{a_2 + c_1 q^2 + c_2 q^4} \tag{2}$$

where $\langle(\Delta\rho)^2\rangle$ is the mean square fluctuation of the scattering length density and a_2, c_1, c_2 are the coefficients originating from the expansion of the free energy of the system in terms of order parameter and its derivatives (for details, see Ref. [3]). At high q-region, this function behaves like q^{-4}.

The coefficients a_2, c_1, c_2 are related to the two characteristic lengths, by

$$D = 2\pi\left[\frac{1}{2}\left(\frac{a_2}{c_2}\right)^{1/2} - \frac{1}{4}\frac{c_1}{c_2}\right]^{-1/2} \tag{3}$$

and

$$\zeta = \left[\frac{1}{2}\left(\frac{a_2}{c_2}\right)^{1/2} + \frac{1}{4}\frac{c_1}{c_2}\right]^{-1/2} \tag{4}$$

The scattering profiles obtained from fitting experimental data to Teubner–Strey formula (with polychromaticity of neutrons taken into account) are also shown in Figs. 1 and 2. Except for the sample fully swollen in D_2O the fits are very good in the whole experimental q-range. For the sample swollen fully in D_2O, the fitting was less satisfactory for $q > 0.15$ Å^{-1} due to somewhat steeper decay of the scattering intensity ($I \propto q^{-4.4}$) in this region. The values of the three parameters of the model, D, ζ and $\langle(\Delta\rho)^2\rangle$, determined from fitting are given in Table 6.

In the samples partially swollen in D_2O the persistence length ζ obtain values 21–22 Å. For the fully swollen sample somewhat lower value was determined ($\zeta = 17$ Å), however, this fact may be also a consequence of somewhat worse fitting of data to the Teubner–Strey formula. The worse fitting is also reflected in too high value of $\langle(\Delta\rho)^2\rangle$

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[1] To be precise, partial volume fractions of the components should be used in the calculations. Unfortunately, values of this parameters are not available for the present system. However, for a reasonable estimation of scattering properties of the phases volume fractions can be used.

[2] Unfortunately, the KNO_3 concentration inside the swollen samples is not available, however, its influence on the neutron scattering properties of the phases can be neglected.

Table 5
Parameters calculated assuming model two-phase structure (model II): phase A = $D_2O(+KNO_3)$ + POE, phase B = POP + PDGEBA. The same symbols as in Table 3.

Sample	v_A	v_B	$\lvert\rho_A - \rho_B\rvert\ 10^{10}$ (cm^{-2})	$\langle(\Delta\rho)^2\rangle\ 10^{20}$ (cm^{-4})	$Q\ 10^{20}$ (cm^{-4})
EP115 + D_2O (fully swollen)	0.543	0.457	4.00	3.96	78.2
EP115 + D_2O (part. swollen)	0.480	0.520	3.60	3.23	63.9
EP115 + D_2O (part. swollen)	0.370	0.630	2.60	1.57	31.0
EP115 + 0.01 M KNO_3	0.463	0.537	3.47	3.00	59.2
EP115 + 0.02 M KNO_3	0.467	0.533	3.50	3.05	60.3
EP115 + 0.05 M KNO_3	0.456	0.544	3.43	2.91	57.5
EP115 + 0.10 M KNO_3	0.475	0.525	3.57	3.17	62.6

Table 6
Values of the parameters obtained by fitting according to the Teubner–Strey model: persistence length, ξ, periodicity, D, and mean square density fluctuation of the scattering length density, $\langle(\Delta\rho)^2\rangle$. Q_{TS} is the scattering invariant calculated by $Q_{TS} = 2\pi^2\langle(\Delta\rho)^2\rangle$.

Sample	ξ (Å)	D (Å)	$\langle(\Delta\rho)^2\rangle\ 10^{20}$ (cm^{-4})	$Q_{TS}\ 10^{20}$ (cm^{-4})
EP115 + D_2O (fully swollen)	17	73	7.51	148.3
EP115 + D_2O (part. swollen)	21	57	3.13	61.8
EP115 + D_2O (part. swollen)	22	49	0.89	17.5
EP115 + 0.01 M KNO_3	19	57	4.36	86.0
EP115 + 0.02 M KNO_3	19	55	4.09	80.7
EP115 + 0.05 M KNO_3	20	54	3.72	73.3
EP115 + 0.10 M KNO_3	20	52	3.12	61.6

and scattering invariant Q_{TS} obtained for this sample (compare with the experimental value, given in Table 2). For partially swollen samples the fits are better in the whole q-range and the values of the scattering invariant determined, Q_{TS}, are close to the experimental ones. The periodicity D obtains values decreasing from ca. 73 Å (fully swollen sample) to 49 Å (the lowest content of D_2O) reflecting shrinkage of the water-rich phase.

Similarly, for the samples swollen in KNO_3 solutions, the fits are very good which is also reflected in the small difference between the model and experimental values of the scattering invariant. The persistence length does not change too much with KNO_3 concentration in the swelling solution obtaining values ζ = 19–20 Å, comparable to the value determined for the hydrogel swollen in D_2O to similar degree (ζ = 21 Å, see Table 6). Unlike this, the periodicity D decreases strongly with increasing KNO_3 concentration obtaining values D = 73 Å (sample swollen fully in D_2O), 57 Å (swelling in 0.01 M KNO_3) and 52 Å (swelling in 0.1 M KNO_3).

The drop of the periodicity (as well as the decrease of the Bragg distance) with increasing KNO_3 concentration at almost constant swelling degree means that nanophase separated structure of these hydrogels becomes finer. Interaction of POE with water in hydrogels as well as aqueous solutions depends strongly on the number and strength of hydrogen bonds in unit volume of the system [12]. In D_2O, potassium nitrate dissociates completely to potassium cations and (much bigger) nitrate anions. Mainly nitrate anions are breaking deuterium bonded structure of D_2O and make POE–D_2O interaction more favourable [13]. Therefore, when KNO_3 is present in the swelling solution more POE is dragged into the water-rich phase (transfer of POE) and scattering properties of hydrogels shift from the model II to model I. The nanophase separated structure becomes finer since the number of POE–D_2O is increased, too. This is in accordance with observations made on swelling behaviour of POE hydrogels in aqueous solutions of inorganic salts [14].

4. Conclusions

A series of epoxy hydrogels swollen to various degrees was prepared by swelling of hydrophilic non-stoichiometric epoxy network and investigated by SANS. Degree of swelling was controlled in two ways: by partial evaporation of the solvent (D_2O) and by concentration of inorganic salt (KNO_3) in the swelling solution.

Using SANS, nanophase separated structure consisting of the water-rich and water-poor phases was confirmed in all hydrogels. Experimental values of scattering invariant lie in the limits expected for two models corresponding to the absence or full presence of POE in the water-rich phase.

Scattering data from hydrogels are fitted satisfactorily to the Teubner–Strey model assuming bicontinuous locally lamellar structure and values of the three structural parameters of the model: the periodicity, D, persistence length, ζ, and the mean square fluctuation of the scattering length density, $\langle(\Delta\rho)^2\rangle$, were determined by fitting.

The analysis showed that drying of the fully swollen hydrogel causes the shrinkage of both phases accompanied by dragging more POE into the water-rich phase. In the region of concentrations used, the hydrogels prepared using KNO_3 solutions contain almost equal amount of D_2O. This is confirmed by almost the same incoherent background in high q-region of the scattering profiles, however, the profiles differ in low q-region and depend on the concentration of KNO_3. The scattering data are consistent with idea that nanophase separation becomes finer as more POE is dragged into the water-rich phase due to the improvement of the POE-interaction resulting from breakage of the deuterium-bonded structure of D_2O by large nitrate anions in the swelling solution.

To conclude, the SANS results obtained provide a valuable information about the nanophase separated structure of epoxy hydrogels. The information will be useful in interpretation of the results obtained from these systems by other methods such as, e.g., differential scanning calorimetry.

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