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Structure and swelling behaviour of hydrophilic epoxy networks investigated by SANS

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Abstract

Structure of hydrophilic epoxy networks swollen in deuterated water has been investigated by small-angle neutron scattering (SANS). Two series of the networks were prepared by end-linking reaction of α,ω-diamino terminated poly(oxypropylene)-*block*-poly(oxyethylene)-*block*-poly(oxypropylene) (POP–POE–POP), α,ω-diamino terminated poly(oxypropylene) (POP) and diglycidyl ether of Bisphenol A propoxylate (PDGEBA). In the first series, prepared using functionalized POP–POE–POP and PDGEBA, hydrophilicity of the networks was controlled via cross-linking density of the networks, changing the initial ratio of reactives. In the second series, POP–POE–POP was gradually substituted by POP of the same molecular weight, enabling a control of hydrophilicity of the networks at essentially constant crosslinking density in this way. Microphase separated structure of the networks swollen in deuterated water with composition variations on nanometer scale was found by SANS. The scattering data were fitted to the Percus–Yevick model, approximating the swollen network by an idealized system of spheres dispersed in the matrix. Satisfactory fits in the region of the interference scattering peak were obtained giving values 30–70 Å for the average radius of the spherical regions. Radius of the spheres increases with increasing hydrophobicity of the networks (growing POP content and/or network crosslinking density).

Keywords: Epoxy network; Swelling; Small-angle neutron scattering

1. Introduction

Epoxy resins belong to a very important class of industrial polymer materials due to their excellent mechanical, thermal and dielectric properties. They are widely employed in many important applications such as surface coatings, structural adhesives and advanced composites in electronic or aerospace industries [1].

Epoxy resins are usually prepared by the reaction of diamino-functionalized prepolymer with a diepoxide, e.g. α,ω-diamino terminated polyoxypropylene (POP) with diglycidyl ether of Bisphenol A (DGEBA), during which the initially liquid reaction mixture passes through a gel-point and solidifies into the polymer network. By using α,ω-diamino terminated polyoxyethylene (POE) hydrophilic networks can be prepared; however, high reactivity of amino groups in this case can be a disadvantage in some applications. α,ω-diamino terminated poly(oxypropylene)-*block*-poly(oxyethylene)-*block*-poly(oxypropylene)s (Jeffamine® ED series) are less reactive and epoxy networks prepared from them have properties which can be attractive for biomedical applications.

Structure of epoxy networks prepared using a mixture of Jeffamines and diepoxide has been investigated by a number of authors. In our previous report [2], a series of hydrophilic epoxy networks of various stoichiometry was prepared by reaction of the α,ω-diamino terminated triblock POP–POE–POP and diglycidyl ether of brominated Bisphenol A (Br-DGEBA). The networks were studied in the dry and swollen state by dynamic mechanical analysis (DMA), small- and wide-angle X-ray scattering (SAXS and WAXS) and differential scanning calorimetry (DSC). While, a microphase separated structure without well-defined boundaries between phases was found in dry networks, swelling of the networks in water leads to a formation of distinct microphase separated hydrophobic and hydrophilic domains. Former ones consist mainly of diepoxide chains, latter ones of a mixture of hydrophilic POE blocks with water. In Ref. [2], the brominated

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diepoxide was used to provide a sufficient contrast for SAXS and is not used normally in preparation of epoxies for practical applications. On the other hand, structure of polymer networks in swollen state can be also investigated by small-angle neutron scattering (SANS) if a deuterated solvent is used. SANS has been already used in the research of swollen polymer networks (polymer gels) for quite a long time.

SANS results obtained from neutral polymer networks swollen in good solvents [3–10] have shown that SANS intensity decays monotonously with increasing magnitude of scattering vector. In principle, the decay consists of two parts characterized by two correlation lengths. The shorter correlation length is attributed to the dynamic fluctuations in polymer network segment density due to their thermal agitation, the longer one is considered as being a manifestation of frozen static fluctuations formed during the cross-linking reaction. In the case of the network containing short chains which swell to lower degree, both regions can merge and become indistinguishable each of other [11,12].

On the other hand, charged gels exhibit the behaviour very different from that of the neutral gels. Scattering becomes to be very sensitive to temperature and non-monotonous with a distinct scattering peak [13,14]. This is attributed to the microphase separation due to worsening of the polymer–solvent interaction with increasing temperature. A review of SANS results obtained on various swollen polymer networks can be found in Ref. [15].

Structure of aqueous solutions of neutral polymer systems, such as block copolymers of POE and POP (pluronics, tetronics, etc.) is also well-known to be very sensitive to temperature. An interesting thermodynamic behaviour of aqueous solutions of the block copolymers of this kind can be transferred into networks by their cross- or end-linking. Our primary concern in this paper is to investigate by means of SANS the structure of the epoxy networks prepared using diamino terminated POP–POE–POP and POP swollen in deuterated water. Diglycidylether of Bisphenol A propoxylate (PDGEBA) was used as an end-linking agent since it suits much better for practical applications than Br-DGEBA.

2. Experimental

2.1. Materials

In the preparation of networks, α,ω-diamino terminated poly(oxypropylene)-*block*-poly(oxyethylene)-*block*-poly(oxypropylene) (Jeffamine® ED2003, Huntsman), α,ω-diamino terminated poly(oxypropylene) (Jeffamine® D2000, Huntsman) and diglycidyl ether of Bisphenol A propoxylate (PDGEBA, Fluka) were used. Molecular weights of both, ED2003 and D2000, are ca 2000 g mol^{-1}. POE content in ED2003 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 ED2003 and D2000 determined by titration were $c_{\mathrm{NH2}}=0.95\times10^{-3}$ mol g^{-1} and 1.00×10^{-3} mol g^{-1}, respectively. Concentration of epoxy groups in PDGEBA determined by titration was $c_{\mathrm{E}}=2.92\times10^{-3}$ mol g^{-1}.

Table 1
Initial molar ratio r, ($r=2[\mathrm{NH}_2]_0/[\mathrm{E}]_0$), of the reactives used in the preparation of the Series A and weight fraction of sol, w_{S}

Sample	R	w_{S}
EP1	1.00	0.21
EP2	1.12	0.15
EP3	1.25	0.17
EP4	1.50	0.30
EP5	2.00	0.50

Two series of epoxy networks were prepared. In Series A, ED2003 and PDGEBA was used, at initial molar ratio of reactive groups, r, $r=2[\mathrm{NH}_2]_0/[E]_0=1.00$, 1.12, 1.25, 1.50, 2.00 (samples EP1, EP2, EP3, EP4, EP5, see Table 1), where $[\mathrm{NH}_2]_0$, and $[\mathrm{E}]_0$ 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.

In Series B, part of ED2003 was substituted by D2000 at constant initial molar ratio of reactive groups $r=1.00$. Degree of substitution was characterised by parameter p, $p=m_{\mathrm{ED2003}}/(m_{\mathrm{ED2003}}+m_{\mathrm{D2000}})$, m_{ED2003} and m_{D2000} being the weights of ED2003 and D2000, respectively. ED2003 and D2000 were first stirred at 100 °C to melt all ED2003 till clear liquid mixture was obtained. Then PDGEBA was added and the system was stirred at the same temperature for about 15 min and poured into Teflon moulds. Series of networks with $p=0$, 0.1, 0.3, 0.5, 0.7 and 0.9 (samples EP21, EP22, EP23, EP24, EP25 and EP26, see Table 2), were prepared in this way.

Curing reaction of all systems in both series proceeded at 120 °C for 48 h in nitrogen atmosphere. Due to their hydrophilicity, all networks were stored in a desiccator and dried at 50 °C in vacuum oven before further investigation. All the networks were transparent.

2.2. Measurements

2.2.1. Extraction and swelling

The weight fractions of sol were determined from the weight decrease after a triple extraction of the samples in toluene at room temperature. After the extraction the samples were dried, first in air, later in vacuum oven at 70 °C for 48 h and the weight in the dry state was measured. Values of the weight fraction of sol, w_{S}, determined from the weight decrease

Table 2
Content of ED2003 in the mixture of diamines, p, ($p=m_{\mathrm{ED2003}}/(m_{\mathrm{ED2003}}+m_{\mathrm{D2000}})$), used in the preparation of the Series B and weight fractions of sol, w_{S}

Sample	P	w_{S}
EP1	0	0.21
EP26	0.1	0.24
EP25	0.3	0.15
EP24	0.5	0.15
EP23	0.7	0.12
EP22	0.9	0.13
EP21	1	0.10

Table 3
Densities, *d*, and neutron scattering length densities, *ρ*, of the components at 25 °C

Compound	*d* (g cm^{-3})	$\rho\times10^{10}$ (cm^{-2})
POE	1.08	0.61
POP	1.01	0.35
PDGEBA	1.09	1.15
D_2O	1.10	6.34

are given in Tables 1 and 2. Dry samples were swollen in various solvents (distilled water, toluene, carbon tetrachloride and benzene) at 20 °C and periodically removed, surface-dried and quickly weighed. Equilibrium swelling ratio *Q*, was calculated as the ratio of the weight of swollen sample, *m*, and that of dry sample after extraction before swelling, m_0.

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 [16]. A mean neutron wavelength $\lambda=4$ Å, and sample-detector distances 1.3 and 4 m were used, covering the range of the magnitudes of scattering vector 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 acquisition times were about 10 min for each sample at each detector position. The samples were thermostated at 25.0 ± 0.1 °C. Immediately before the measurements, samples swollen to equilibrium in the solvent were transferred into 2 mm thick measuring quartz cells filled with the same solvent. Some swollen samples were also measured between two thin polyethylene foils (of thickness ca 40 μm). The scattering intensities were radially averaged and corrected for the sample transmission, room background and detector efficiency using standart procedures. Evaluation of experimental data was carried out by self-written procedures in MATLAB. Values of the density, *d*, and neutron scattering scattering length density, *ρ*, at 25 °C of the components of epoxy networks studied are given in Table 3.

3. Results and discussion

Fig. 1 shows the dependence of the swelling ratio, Q_{sw}, in various solvents on the initial molar ratio of the reactives, *r*, for Series A. It can be seen that for all solvents used (deuterated water, toluene, benzene and carbon tetrachloride) swelling is the lowest in proximity of $r\approx1.12$. This composition is closest to the stoichiometric network and is caused probably by uncertainty in determination of amino and/or epoxy group concentration. The networks with $r\neq1.12$ are out of stoichiometry and consequently of lower cross-linking density and able of higher swelling. For $r>1.15$, the degree of swelling increases in the solvent order: toluene, water, carbon tetrachloride and benzene. For $r<1.15$, swelling ratio increases in order: water, toluene, carbon tetrachloride and benzene. The interchange of water and toluene can be attributed to the increasing content of the hydrophilic component (ED2003) in the networks.

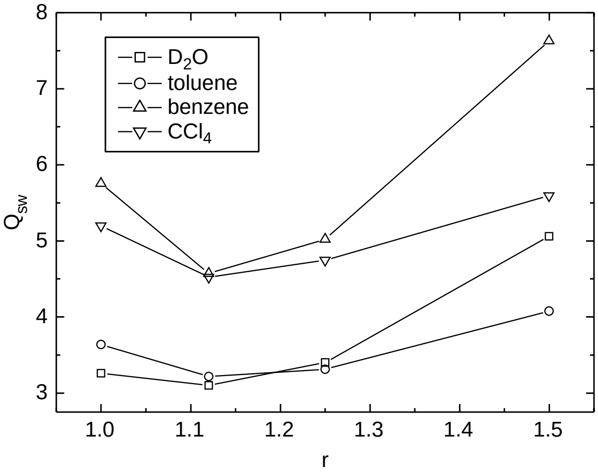

Fig. 1. Dependence of swelling ratio, Q_{sw}, of the networks Series A on initial molar ratio of reactives, *r*.

Swelling behaviour of the networks in Series B is illustrated in Fig. 2. This series corresponds to approximately constant cross-linking density as molecular weights of ED2003 and D2000 are close, being ca 2000 g mol^{-1}. All dependences are monotonous, and (except for the network EP1 with $p=1$), swelling increases in the order: water, toluene, benzene and carbon tetrachloride. Values of the swelling degree obtained for the networks in Series B in toluene are almost constant, which means that interaction of ED2003 and D2000 with this solvent is very similar. Swelling of the networks in water and toluene increases with increasing substitution of D2000 by ED2003, consequently, these solvents are better for ED2003 than D2000. For swelling in carbon tetrachloride, descending dependence of Q_{sw} with content of ED2003 was obtained, therefore, this solvent is worse for ED2003 than D2000.

Fig. 3 presents SANS patterns from the networks in Series A swollen in deuterated water. Except for the network EP5 with highest swelling ratio, a distinct scattering peak was found. The position of the peak shifts very slightly to higher *q*-region with increasing *r*.

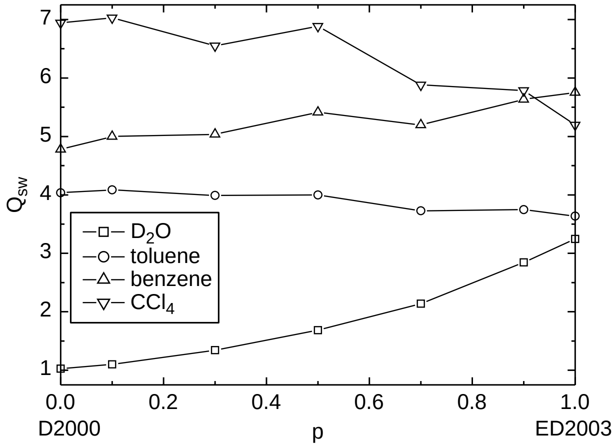

Fig. 2. Dependence of swelling ratio, Q_{sw}, of the networks Series B on the ED2003 content in diamine mixture, *p*.

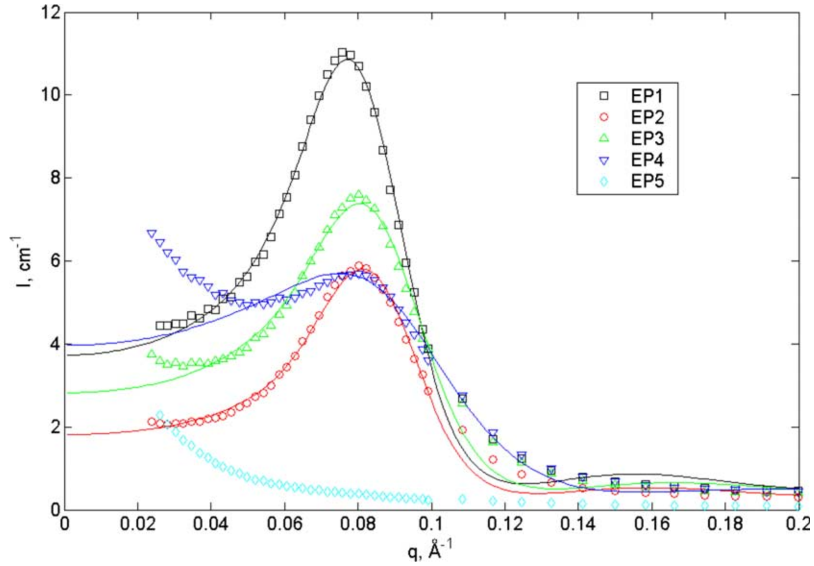

Fig. 3. SANS scattering profiles (scattering intensity I vs. magnitude of the scattering vector q) obtained from networks Series A swollen in D_2O at 25 °C. Solid lines represent fits according to Percus–Yevick model.

Scattering patterns obtained for networks Series B swollen in deuterated water are shown in Fig. 4. Except for the network that swells the least (EP21) a distinct scattering peak is found again. With decreasing content of hydrophilic ED2003 (and, consequently, decreasing swelling ratio in this solvent), the position of peak shifts considerably to lower q-region. Peak positions, $q_{\max}$, and corresponding values of the Bragg distance D_B, defined by $D_B = 2\pi/q_{\max}$, for both series are summarized in Tables 4 and 5. From these results it can be concluded that after swelling almost all the systems (except for EP5 and EP21) are microphase separated with characteristic variation of the neutron scattering length density on the scale of 80–150 Å.

To obtain more information about the microphase separated structure, values of the scattering invariant, Q, were calculated by numerical integration of the experimental SANS patterns from which incoherent background was subtracted (see Tables 4 and 5). As the primary neutron beam is moderately polychromatic due to the transmission function of the velocity selector, this circumstance has to be taken into account. In Appendix, formulas for experimental smearing of scattering patterns and change of the scattering invariant due to the polychromaticity of the primary beam are given. In the calculations presented in this paper, normal distribution of neutron wavelength was used to this purpose with the ratio of standard deviation to mean value of wavelength $\Delta\lambda/\lambda = 0.08$–$0.11$ [16]. Thus, smearing due to polychromaticity of this extent leads ca 3% increase in the values of scattering invariant (see Eq. (A7) in Appendix A).

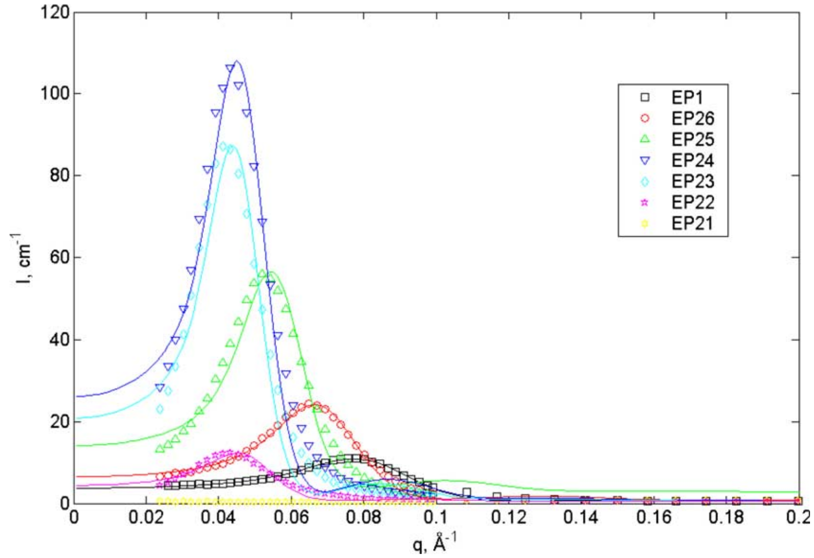

Fig. 4. SANS scattering profiles obtained from networks Series B swollen in D_2O at 25 °C. Solid lines represent fits according to Percus–Yevick model.

Table 4
SANS parameters obtained for Series A

Sample	$q_{\max}$ (Å^{-1})	D_B (Å)	Q (exp.) $\times 10^{20}$ (cm^{-4})	v_{POE}	v_{POP}	v_{PDGEBA}	v_{D2O}	Q(th.) $\times$ 10^{20} (cm^{-4})
EP1	0.076	83	30	0.113	0.080	0.121	0.686	132
EP2	0.080	79	19	0.124	0.088	0.118	0.670	137
EP3	0.080	79	25	0.117	0.083	0.101	0.699	131
EP4	0.080	79	25	0.084	0.060	0.060	0.796	101

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.); volume fractions of polyoxyethylene, v_{POE}; polyoxypropylene, v_{POP}; diglycidylether of Bisphenol A propoxylate, v_{PDGEBA}; deuterated water, v_{D2O}; in swollen networks, value of the scattering invariant assuming water forms one-phase of two-phase model, Q (th.).

Table 5
SANS parameters obtained for Series B

Sample	$q_{\max}$ (Å^{-1})	D_B (Å)	Q (exp.) $\times 10^{20}$ (cm^{-4})	v_{POE}	v_{POP}	v_{PDGEBA}	v_{D2O}	Q (th.) $\times 10^{20}$ (cm^{-4})
EP1	0.076	83	30	0.113	0.080	0.121	0.686	132
EP26	0.065	97	43	0.115	0.105	0.138	0.642	142
EP25	0.052	121	50	0.118	0.175	0.184	0.523	155
EP24	0.043	146	53	0.106	0.264	0.233	0.397	150
EP23	0.041	153	38	0.079	0.384	0.293	0.244	117
EP22	0.050	126	8	0.032	0.528	0.354	0.086	50

The same symbols as in Table 4.

The polychromaticity corrected values of the scattering invariant can be compared with theoretical ones using the simplest two-density model assuming complete separation of deuterated water from the polymer phase

$$Q = 2\pi^2 v_{D2O}(1 - v_{D2O})(\rho_{D2O} - \rho_p)^2 \qquad (1)$$

where v_{D2O} and ρ_{D2O} are volume fraction and neutron scattering length density of water and ρ_p is neutron scattering length density of the polymer phase. Value of ρ_p was estimated as a volume average

$$\rho_p = \frac{v_{POE}\rho_{POE} + v_{POP}\rho_{POP} + v_{PDGEBA}\rho_{PDGEBA}}{v_{POE} + v_{POP} + v_{PDGEBA}} \qquad (2)$$

where v_i and ρ_i are volume fractions and neutron scattering length densities of the components of the polymer phase.

Experimental values of the scattering invariant obtained are smaller than the values calculated using the two-density model, therefore, a phase consisting only of water cannot be formed in the system, if the model is applicable.

Before discussing the possible structures of the networks in swollen state it will be useful to recall topology of epoxy networks. One of the characteristic features of the reaction between a diamine and a diepoxide consists in that in the course of the curing process diepoxide molecules are linked into long chains (see Fig. 5). Diamine chains are grafted to these diepoxide chains by one or both ends. Length distribution and its moments (polymerization degrees) of diepoxide molecules is similar to that obtained in radical polymerization and can be calculated, e.g. using theory of branching processes (see Appendix B). In stoichiometric network ($r = 1$), PDGEBA molecules are linked to very long chains, shorter chains are formed with growing non-stoichiometry ($r > 1$), see Figs. 5 and 6. Space distribution of PDGEBA chains in the volume of the system is almost uniform since only low degree of microphase separation was found in similar systems [17].

When water is absorbed by the networks and microphase-separated structure formed, topology of the epoxy network in such a microphase separated swollen state dictates that PDGEBA chains as the hydrophobic constituent of the system should form a continuous phase. Otherwise, collapse of the PDGEBA chains into globules would require non-realistic rearrangements of grafted ED2003 (and D2000) chains. Only when PDGEBA chains are shorter and number of ED2003 grafted to PDGEBA only by one end increases, formation of particulate phase is possible. This can happen at higher values of r (see Fig. 6).

Therefore, it can be expected that for almost all samples hydrophobic phase is penetrated by cells filled by water and (expanded) hydrophilic PEO chains (see Fig. 7). The cells can

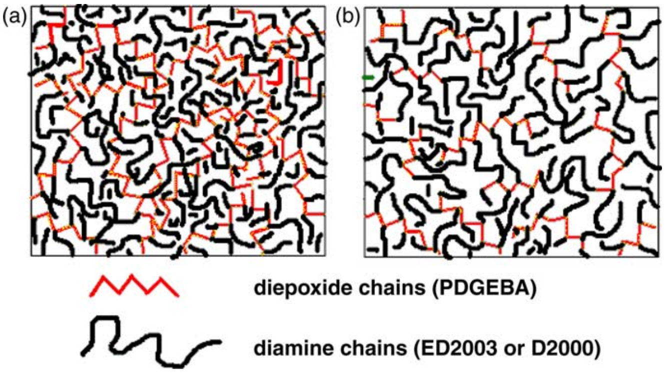

Fig. 5. Schematic of the structure of epoxy networks in dry state: (a) stoichiometric network, (b) network out of stoichiometry.

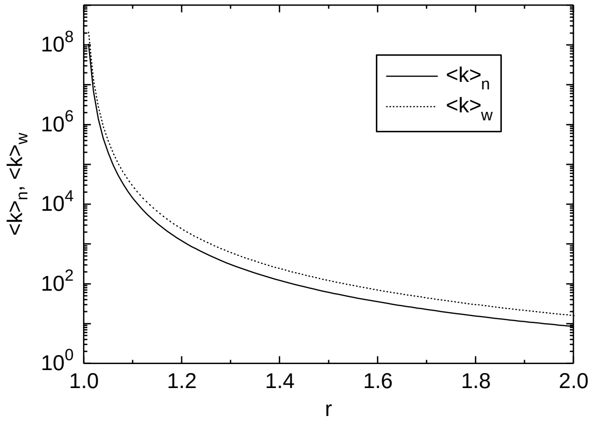

Fig. 6. Dependence of the number and weight average of the polymerization degree of PDGEBA chains in epoxy networks.

be isolated or interconnected. The free energy of such the system will decrease with growth of the size of the cells decreasing the number of unfavourable contacts between water and hydrophobic part in this way. On the other hand, this growth is accompanied by the extension of PEO chains leading to an increase of the free energy. The resulting size of the cells will be therefore governed by an interplay of these two factors with the length of PEO blocks in fully expanded state being upper limit.

To obtain more detailed information about the structure of the systems investigated by SANS a suitable model providing a formula for scattering intensity or structure factor is necessary. The only microphysical model available at the moment is the Panyukov-Rabin model [18,19]. This model exploits information about the network chains (effective segment length and the number of segments), polymer-solvent interaction (Flory–Huggins parameter) and macroscopic degree of swelling as input parameters. In its generalized version for charged gels [20] has been already used for interpretation of SANS data from hydrogels based on poly(*N*-isopropylacrylamide) by Shibayama et al. [21–23].

However, we have found that Panyukov–Rabin model is not appropriate for satisfactory fitting of our experimental data. It fails mainly due to its inability to cope with the right side of the scattering peaks where (smeared) intensity decays as q^{-n} with $n \approx 5$–8 depending on the system. Therefore, we have resigned from a molecular description of the microphase separated structure and used more descriptive approach based on the Percus–Yevick (PY) model [24]. This model has been used successfully in the interpretation of SAXS/SANS data from various microphase separated polymer systems, see, e.g. Refs. [25–27]. Since expected structure is rather complicated, the hydrophilic cells mentioned above (Fig. 6) are approximated by spheres of a uniform radius R interacting via hard-sphere potential and dispersed in the matrix of the hydrophobic phase.

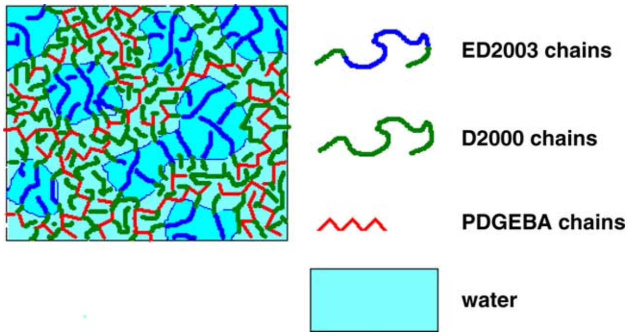

Fig. 7. Schematic of the microphase separated structure of the epoxy networks in swollen state.

Scattering cross-section per unit volume from such system is given by

$$I(q) = (\rho_1 - \rho_2)^2 n V_p^2 P(qR) S(qR_{\mathrm{HS}}, \nu_{\mathrm{HS}}) \tag{3}$$

where ρ_1 and ρ_2 are scattering length densities of the phases (whose composition is not assumed a priori), n is number concentration of spheres, $V_{\mathrm{p}} = 4\pi R^3/3$ is volume of the spheres, ν_{HS} is volume fraction of the hard spheres with (interaction) radius R_{HS}, P and S are the sphere form factor and Percus-Yevick structure factor, respectively. Expressions for P and S can be found, e.g. in Ref. [25]. To keep the number of fitting parameters at reasonable level, we put the spheres radius to be equal to the hard-sphere interaction radius, i.e., $R = R_{\mathrm{HS}}$. Figs. 3 and 4 show that Percus–Yevick model describes plausibly well SANS patterns in the q-region around the scattering peak. Values of the three fitting parameters ($|\rho_1$-$\rho_2|$, R_{HS} and ν_{HS}) determined are given in Tables 6 and 7.

From a comparison of the values of the difference in scattering length densities with values for the components of the system at 25 °C, (see Table 3), it can be concluded that water has to be prevailing component in one of the phases as it is expected. Comparing the values of ν_{HS} with the values of volume fraction of water in the systems leads to the conclusion that certain amount of water must be present also in the other phase. From the values determined for the radius of hard spheres it follows that hard sphere domains grow with decreasing content of ED2003 and, consequently, increasing hydrophobicity of the system, both, in Series B as well as in Series A (despite of the increasing cross-linking density). This is in agreement with our considerations described above. The highest diameter found by fitting ($2R = 154$ Å) is closed to the length of ED2003 chain in fully stretched state (ca 170 Å).

Fitting outside the region of the scattering peak is less satisfactory due to extreme simplicity of the model and increasing sensitivity of the scattering on the structural details of the system. An increase of the scattering observed in the low q-region in Series A indicates that microphase separation

Table 6
Values of the parameters obtained by fitting according to the Percus–Yevick model for Series A

Sample	$\lvert\rho_1 - \rho_2\rvert \times 10^{10}$ (cm^{-2})	R_{HS} (Å)	ν_{HS}
EP1	2.9	38	0.39
EP2	2.2	37	0.41
EP3	2.6	36	0.37
EP4	2.9	30	0.24

Difference in neutron scattering length densities between spheres and matrix, $|\rho_1 - \rho_2|$, hard-sphere radius, R_{HS}, volume fraction of hard spheres, ν_{HS}.

Table 7
Values of the parameters obtained by fitting according to the Percus–Yevick model for Series B

Sample	$\|\rho_1-\rho_2\|\times 10^{10}$ (cm^{-2})	R_{HS} (Å)	v_{HS}
EP1	2.9	38	0.39
EP26	3.3	46	0.43
EP25	3.6	58	0.46
EP24	3.9	70	0.44
EP23	3.4	71	0.44
EP22	1.4	64	0.38

The same symbols as in Table 5.

occurs also on much larger space scale. In the high q-region the PY model curves become more structured than monotonous experimental decays found. Introduction of the sphere polydispersity and/or surface roughness would definitely suppress the oscillations of the PY scattering curves in high q-region [28] and lead to better fits, however, we resigned from further refining of the model due to lack of necessary information. Nevertheless, we think that the fitting using the simplest employment of PY model provides at least a qualitative information about the structure of the systems investigated.

The network of highest deviation from stoichiometry and highest swelling ratio (EP5, $r=2$) is the only one without scattering peak in the q-region investigated. We think that unlike the rest of the samples, this system is more homogeneous exhibiting dynamic and static fluctuations in density reflected in scattering profile which might be described by formulas given in Refs. [4,5].

4. Conclusions

Two series of the hydrophilic epoxy networks were prepared and investigated by SANS. In the first series, hydrophilicity was controlled by cross-linking density, in the second one by relative content of POE and POP at constant crosslinking density. Microphase separated structure of all networks swollen in deuterated water was revealed by SANS. One-phase is rich in water and hydrophilic polymer (POE) while the other consists of the hydrophobic constituents (PDGEBA and POP) swollen by water to smaller degree. Characteristic length of the composition variations resulting from the variations of the neutron scattering length density is on the scale of 80-150 Å. Further analysis and interpretation of SANS results were performed using Percus–Yevick model. In the model the structure of the swollen networks is replaced by an idealized two-phase structure consisting of uniform spheres of one-phase dispersed in the matrix of the other phase. Average radius of the water rich domains (30–70 Å) was found to increase with increasing hydrophobicity of the networks (growing POP content and/or crosslinking density) . To conclude, the SANS results obtained provide a valuable information about the nanostructure of the epoxy networks swollen in water. This information will be useful in interpretation of the results obtained from these systems by other methods such as, e.g. differential scanning calorimetry [29].

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Appendix A. Correction of the scattering invariant to polychromaticity of the primary beam

In the case of the polychromatic primary beam, the relation between smeared and original scattering intensity profiles is given by [30]

$$\tilde{I}(q)=\int_0^\infty K(\lambda)I\left(q\frac{\lambda_0}{\lambda}\right)\mathrm{d}\lambda \tag{A1}$$

where $I(q)$ corresponds to the scattering obtained using monochromatic primary beam of a (reference) wavelength λ_0, and $K(\lambda)$ is the distribution function of the wavelengths normalized by

$$\int_0^\infty K(\lambda)\mathrm{d}\lambda=1 \tag{A2}$$

Correction for beam polychromaticity, i.e. solution of the Eq. (A1) with respect to $I(q)$ has been given by Svergun and Semenyuk [30]. To simplify the notation, let us re-scale wavelength with respect to the reference wavelength λ_0, i.e. introduce a new variable λ' by $\lambda'\equiv\lambda/\lambda_0$. Then Eq. (A1) obtains form

$$\tilde{I}(q)=\int_0^\infty K(\lambda')I(q/\lambda')\mathrm{d}\lambda' \tag{A3}$$

On taking the Mellin transform of both sides of the last equation one gets

$$\begin{aligned}\int_0^\infty \tilde{I}(q)q^{s-1}\mathrm{d}q&=\int_0^\infty\left[\int_0^\infty K(\lambda')I(q/\lambda')\mathrm{d}\lambda'\right]q^{s-1}\mathrm{d}q\\&=\int_0^\infty \lambda' K(\lambda')\left[\int_0^\infty I(q/\lambda')\left(\frac{q}{\lambda'}\right)^{s-1}d\left(\frac{q}{\lambda'}\right)\right]\lambda'^{s-1}\mathrm{d}\lambda'\end{aligned}$$

and finally

$$\int_0^\infty \tilde{I}(q)q^{s-1}\mathrm{d}q = \int_0^\infty \lambda'^s K(\lambda')\mathrm{d}\lambda' \cdot \int_0^\infty I(q)q^{s-1}\mathrm{d}q \tag{A4}$$

A formula for scattering invariant is obtained by inserting $s=3$ into last equation, hence

$$\int_0^\infty \tilde{I}(q)q^2\mathrm{d}q = \int_0^\infty \lambda'^3 K(\lambda')\mathrm{d}\lambda' \cdot \int_0^\infty I(q)q^2\mathrm{d}q$$

$$= \overline{\lambda'^3} \cdot \int_0^\infty I(q)q^2\mathrm{d}q = \frac{\overline{\lambda^3}}{\lambda_0^3}\int_0^\infty I(q)q^2\mathrm{d}q \tag{A5}$$

For a polychromatic beam with normal distribution of wavelengths characterized by mean wavelength $\bar{\lambda}$ and standard deviation $\Delta\lambda$

$$K(\lambda') = \frac{1}{\sqrt{2\pi}\Delta\lambda}\exp\left[-\frac{1}{2}\left(\frac{\lambda-\bar{\lambda}}{\Delta\lambda}\right)^2\right] \tag{A6}$$

the mean wavelength can be used as the reference ($\lambda_0 = \bar{\lambda}$) and since $\overline{\lambda^3}/\overline{\lambda^3} = 1 + 3(\Delta\lambda/\bar{\lambda})^2$, one obtains

$$\int_0^\infty \tilde{I}(q)q^2\mathrm{d}q = \left[1 + 3\left(\frac{\Delta\lambda}{\bar{\lambda}}\right)^2\right]\int_0^\infty I(q)q^2\mathrm{d}q \tag{A7}$$

Remark. If the full width at half maximum of the wavelength distribution, w_{FWHM}, ($w_{\mathrm{FWHM}} = 2\sqrt{2\ \ln\ 2}\Delta\lambda$) is used as a measure of the polychromaticity, the last equation obtains form

$$\int_0^\infty \tilde{I}(q)q^2\mathrm{d}q = \left[1 + \frac{3}{8\ \ln\ 2}\left(w_{\mathrm{FWHM}}\bar{\lambda}\right)^2\right]\int_0^\infty I(q)q^2\mathrm{d}q \tag{A8}$$

Appendix B. Length distribution of the diepoxide chains

Distribution and its moments (polymerisation degrees) of the diepoxide chains can be estimated simply assuming that reactivity of all reactive places (amino hydrogens and epoxy groups) is equal and does not change in time. Then the distribution is the same as that obtained in radical polymerisation, i.e.

$$n_k = (1-p)p^{k-1}, \quad k = 1, 2, \ldots \tag{B1}$$

where n_k is number fraction of chains in which k epoxide molecules are linked and p is probability of the chain growth. Number $\langle k\rangle_n$ and weight $\langle k\rangle_w$ average of polymerisation degree are given by

$$\langle k\rangle_{\mathrm{n}} = \frac{1}{1-p} \tag{B2}$$

$$\langle k\rangle_{\mathrm{w}} = \frac{1+p}{1-p}, \tag{B3}$$

respectively.

Expression for the probability of chain growth can be obtained by the same procedure as used in Ref. [2], which is based on theory of branching processes and holds

$$p = 1 - \alpha_{\mathrm{BA}}v_{\mathrm{BA}}(1-\alpha_{\mathrm{AB}}) \tag{B4}$$

where v_{BA}, α_{BA} and α_{AB} are extinction probability for bonds originating from epoxy molecule, conversion of epoxy and amino groups, respectively. In the case of excess of amino groups and full conversion of epoxy groups ($\alpha_{\mathrm{BA}}=1$),

$$v_{\mathrm{BA}} = 1 + \frac{r}{2}(\sqrt{4r-3}-3) \tag{B5}$$

and

$$\alpha_{AB} = 1/r \tag{B6}$$

where r is initial molar ratio of reactive groups. Final expression for the probability of chain growth obtains form

$$p = 1 - \left[1 + \frac{r}{2}(\sqrt{4r-3}-3)\right]\left(1-\frac{1}{r}\right). \tag{B7}$$

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