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Small-angle neutron scattering study of nanophase separated epoxy hydrogels

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ABSTRACT

A series of hydrophilic epoxy networks was prepared by end-linking reaction of α,ω-diamino terminated poly(oxypropylene)-*block*-poly(oxyethylene)-*block*-poly(oxypropylene) of average molar mass ca. 600 g mol^{-1} and diglycidyl ether of Bisphenol A propoxylate at various values of stoichiometric ratio, r, of amino to epoxy groups. Epoxy hydrogels were obtained by swelling of the epoxy networks in deuterated water. Nanophase separated structure of all hydrogels has been revealed by small-angle neutron scattering. The structure is much finer than that found in the similar system investigated previously which was prepared using much longer diamine (molar mass ca. 2000 g mol^{-1}). Unlike the previous system, the scattering data from the present system cannot be fitted properly by Percus–Yevick model but Teubner–Strey model based on the locally lamellar order of nanophases dictated by conservation of polymer network topology proves well in the fitting. The values of parameters of the nanophase separated structure – two characteristic lengths: periodicity and persistence length of the locally lamellar order and their dependence on the network composition are determined and analyzed in detail.

1. Introduction

Epoxy resins represent a very important class of polymer materials due to their excellent mechanical, thermal and dielectric properties. They are widely used 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 the reaction, initially liquid reaction mixture passes through a gel-point and becomes solid because a three-dimensional polymer network of macroscopic dimensions is formed.

When a hydrophilic prepolymer, such as, e.g., diamino-functionalized polyoxyethylene (POE) is used in the preparation of the resin, hydrophilic epoxy network is obtained. After immersion in water, the network adsorbs water giving rise to a hydrogel. A question immediately arises: how is water distributed in the volume of hydrogel? Answer to this question on nanometer length scales can be obtained using small-angle neutron scattering (SANS) if deuterated water is used as the swelling agent.

Dependence of the scattering intensity of thermal neutrons on the magnitude of scattering vector q defined by

$$q = \frac{4\pi}{\lambda} \sin\frac{\vartheta}{2}, \tag{1}$$

where λ and ϑ are the wavelength of neutrons and the scattering angle, respectively, reflects fluctuations in the neutron scattering length density in the system under investigation. In a semi-diluted polymer solution in good solvent these fluctuations originate from thermal movement of polymer segments and molecules of solvent mixed on the molecular level leading to a monotonous decay of the scattering intensity, $I(q)$, which can be expressed by [2]

$$I(q) = \frac{kT(\rho_\mathrm{p} - \rho_\mathrm{s})^2 v_\mathrm{p}^2}{K_\mathrm{osm}} \frac{1}{1 + \xi_\mathrm{d}^2 q^2}, \tag{2}$$

where kT is the Boltzmann factor, ρ_p and ρ_s are the neutron scattering length densities of the polymer and solvent, respectively, v_p is the volume fraction of polymer in the solution, K_osm is the osmotic compression modulus of the solution and ξ_d is the polymer screening length (blob size). At high q-region, this function behaves like q^{-2} due to random coil nature of polymer chains in blobs.

Cross-linking of polymer chains into a network leads to the appearance of another, also monotonously decaying, contribution to the scattering intensity caused by fluctuations induced by network junctions [2–9] characterized by another correlation length, ξ_s, $\xi_\mathrm{s} > \xi_\mathrm{d}$. Since both correlation lengths obtain values of 10–100 Å, the swollen polymer networks appear homogeneous on larger length scales.

On the other hand, SANS results obtained from hydrogels, i.e., polymer networks swollen in water, can be very different from

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the above results. Scattering becomes to be very sensitive to temperature and non-monotonous with a distinct scattering peak [10–12]. This observation is attributed to the nano-phase 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. [13].

In our previous paper [14], results of SANS investigation of epoxy hydrogels prepared by swelling of epoxy networks obtained by reaction of diamino-functionalized POE and POP of average molar mass ca. 2000 g mol^{-1} with diglycidyl ether of Bisphenol A propoxylate (PDGEBA) were reported. Nanophase separated structure of all hydrogels was revealed by SANS. The nano-phase separation is caused by a large difference in interaction of water with the constituents of this system: water is good solvent for POE but poor solvent for POP and PDGEBA. A distinct scattering peak was observed in almost all systems investigated and successful fitting of experimental data was achieved by means of the Percus–Yevick model [15].

The SANS results from this system were interpreted on the basis of two-density model of the hydrogel structure concluding that one phase in the system is rich in water and hydrophilic polymer (POE) while the other consists of the hydrophobic constituents (PDGEBA and POP) swollen by a small amount of water. Characteristic length of the composition variations resulting from the variations of the neutron scattering length density was on the scale of 80–150 Å.

In this paper, we investigated structure of a similar system, using diamino-functionalized POP-*b*-POE-*b*-POP copolymer with much shorter POE block. Consequently, the networks prepared have a higher cross-linking degree and lower content of hydrophilic component, and, therefore, a lower degree of swelling in water and higher extent of mutual mixing of hydrophilic and hydrophobic phases in hydrogels are expected. The structure of this system as a function of its composition is investigated by SANS and will be reported and compared with the previous results.

2. Experimental

2.1. Materials

In the preparation of networks 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 $c_{NH2} = 3.2 \times 10^{-3}$ mol g^{-1} and $c_E = 2.92 \times 10^{-3}$ mol g^{-1}, respectively.

Series of epoxy networks was prepared, at compositions described by stoichiometric ratio, *r*, defined as initial molar ratio of reactive groups, $r = 2[NH_2]_0/[E]_0 = 1.00$, 1.06, 1.12, 1.25, 1.50, 1.75 and 2.00 (samples EP111, EP112, EP113, EP114, EP115, EP116 and EP117, see Table 1), where $[NH_2]_0$ 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.

Table 1
Stoichiometric ratios, *r*, in epoxy networks and volume fractions of POE, POP, PDGEBA and D$_2$O in epoxy hydrogels obtained, v_{POE}, v_{POP}, v_{PDGEBA} and v_{D2O}, respectively.

Sample	r	v_{POE}	v_{POP}	v_{PDGEBA}	v_{D2O}
EP111 + D$_2$O	1.00	0.167	0.120	0.626	0.097
EP112 + D$_2$O	1.06	0.164	0.125	0.624	0.087
EP113 + D$_2$O	1.12	0.161	0.123	0.577	0.139
EP114 + D$_2$O	1.25	0.158	0.121	0.512	0.209
EP115 + D$_2$O	1.50	0.126	0.096	0.349	0.429
EP116 + D$_2$O	1.75	0.090	0.069	0.221	0.620
EP117 + D$_2$O	2.00	0.058	0.044	0.132	0.766

Curing reaction of all systems proceeded at 120 °C for 48 h in nitrogen atmosphere. All the networks were transparent.

The networks prepared contain a certain amount of extractable fraction (sol) which has to be removed before swelling and SANS measurements. This was realized by triple extraction of the networks in good solvent (toluene).

2.2. Measurements

2.2.1. Swelling

Epoxy hydrogels were prepared by swelling of dry and extracted networks to equilibrium in D$_2$O at 25 °C. Volume fraction of water in hydrogels, v_{D2O}, was calculated from the mass increase due to water adsorption assuming additivity of volumes as

$$v_{D2O} = \frac{1}{1 + \left(\frac{m}{m_0} - 1\right)\frac{d_{D2O}}{d_0}} \tag{3}$$

where m, and m_0 are masses of the hydrogel and dry extracted network, and d_{D2O} and d_0 are specific masses of deuterated water 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.

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 $\lambda = 4.1$ 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 ($q < 0.02$ Å^{-1}) were excluded from the analysis. The samples were thermostated at 25.0 ± 0.1 °C. Immediately before the measurements, samples swollen to equilibrium in D$_2$O 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

Compositions of the hydrogels investigated are given in Table 1. As expected, the content of water in the hydrogels grows with increasing value of the stoichiometric ratio, *r* (see Table 1), in the initial epoxy networks. This is due to both, decreasing cross-linking degree and increasing amount of the hydrophilic component (POE) at the expense of the hydrophobic ones (POP and PDGEBA) in the epoxy networks.

SANS patterns obtained on the epoxy hydrogels investigated are shown in Fig. 1. The scattering intensity from the hydrogels with very low content of D$_2$O (EP111 and EP112) seem to decay monotonous without a noticeable scattering peak. Hydrogels with higher amounts of D$_2$O (EP113–EP115) show a distinct scattering peak. The Bragg distance, D_B, defined by $D_B = 2\pi/q_{max}$, where q_{max} is the position of scattering peak, obtains values about 70–100 Å. Finally, hydrogels with highest amount of D$_2$O (EP116 and EP117) show an intensive scattering at lowest *q*-region descending monotonously with increasing *q*.