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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, υ_{D_2O}, was calculated from the mass increase due to water adsorption assuming additivity of volumes as

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

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: υ_{POE}, υ_{POP}, υ_{PDGEBA} and υ_{D_2O}, denote the volume fractions of POE, POP, PDGEBA and D_2O, respectively.

Sample	υ_{POE}	υ_{POP}	υ_{PDGEBA}	υ_{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, υ_{D_2O}. Position of the scattering peak, q_{max}, shifts to high q-region and, consequently, Bragg distance,

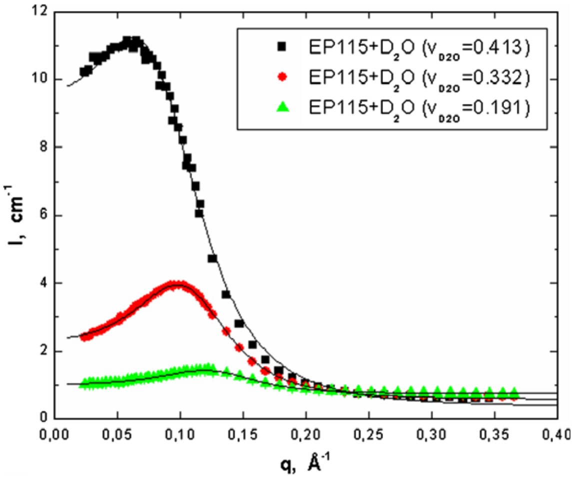

Fig. 1. SANS scattering profiles (scattering intensity I vs. magnitude of scattering vector q) obtained from the partially swollen epoxy network in D_2O at 25 °C. Solid lines represent fits according to Teubner–Strey model.