



Epoxy networks and thermosensitive hydrogels prepared from α,ω -diamino terminated polyoxypropylene and polyoxyethylene bis(glycidyl ether)

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ABSTRACT

A series of stoichiometric hydrophilic epoxy networks was prepared by reaction of α,ω -diamino terminated polyoxypropylene of average molar mass 430, 2000 and 4000 g mol⁻¹ with polyoxyethylene bis(glycidyl ether) of average molar mass 526 g mol⁻¹. The networks were investigated by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). Single glass transitions observed in the networks strongly suggest that the networks present homogeneous single phase, i.e., polyoxypropylene (POP) and polyoxyethylene (POE) are homogeneously built in the network structure. The homogeneity of the networks is also confirmed by absence of a crystallization of POE. Hydrogels obtained by swelling of the networks in water exhibit a strong dependence of swelling degree on temperature. The temperature sensitivity of the hydrogels increases with growing molar mass of the POP used in the network preparation. The swelling behavior of the hydrogel containing POP of highest molar mass (4000 g mol⁻¹) is close to a discontinuity expected at a temperature ca 10–11 °C.

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1. Introduction

Polymer hydrogels are soft materials composed of a hydrophilic polymer network swollen with water. They can be prepared in a number of ways, e.g., by swelling of a dry hydrophilic polymer network in water or crosslinking of a water-soluble polymer in aqueous environment. Structure and properties of hydrogels are result of a delicate interplay between elasticity of polymer network and thermodynamic interaction of polymer with water. As a result,

hydrogels respond very sensitively to changes of external parameters such as temperature, pressure, presence of a cosolvent, surfactant, and ions.

Hydrogels can be tailored regarding their chemical structure, they can be assembled into various structures or integrated into microsystems. Accordingly, hydrogels have become very attractive in modern applications, such as sensors [1,2], actuators [3], microfluidic [4] or microoptical devices [5], and tissue engineering [6].

The most studied hydrogels used in sensor and actuator applications are based on derivatives of polyacrylic acid, such as, e.g., poly(*N*-isopropylacrylamide), prepared by free radical polymerization. However, this method is air-sensitive and difficult to carry out in a controlled fashion in an

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open environment on the small scale. Therefore, to avoid these problems it may be useful to investigate other alternative methods of hydrogel preparation based, e.g., on polycondensation and polyaddition reactions [7].

Polyaddition reaction between di- or triamines and diepoxides is used in production of a class of industrially very important materials - epoxy resins. The reaction is not very sensitive to the presence of water, oxygen or impurities. Due to a broad versatility of chemical structure, excellent mechanical, thermal and dielectric properties epoxy resins have found many applications as adhesives, coatings or castings [8].

In preparation of epoxy resins, hydrophobic reagents are usually used to avoid water absorption that would deteriorate properties of epoxy resins demanded in above applications. On the other hand, when hydrophilic diamines and/or diepoxides are exploited, hydrophilic epoxy resins can be prepared and converted into hydrogels by swelling in water. Swelling behavior of epoxy-based hydrogels can be controlled conveniently by adjusting content of hydrophilic component and network density of the epoxy network.

One of the most important hydrophilic polymers is polyoxyethylene (POE). Diamino terminated triblock copolymers of POE and polyoxypropylene (POP) suitable for preparation of epoxy resins are produced, e.g., by Huntsman under trade name Jeffamine, ED series [9].

POE exhibits a remarkable behavior – in contrast to normal polymer behavior in which the solubility increases with temperature, the solubility of POE decreases with temperature and phase separation occurs above a critical temperature that depends on the molar mass [10]. However, demixing of POE and water is observed at high pressure, only, and at atmospheric pressure POE of molar mass so high as 10^6 g mol⁻¹ is soluble in water from 0 °C to about 100 °C [11], being dominantly hydrophilic in the whole temperature range.

Interaction of POP with water exhibits much dramatic temperature dependence [12]. In water, at atmospheric pressure, POPs of molar masses 1200 and 3000 g mol⁻¹ are soluble only at low concentrations below ca 35 and 18 °C, respectively.

Aqueous solutions of many POE/POP based systems, such as, e.g., POE–POP–POE (pluronics) and POP–POE–POP triblock copolymers have been intensively studied in recent years and very rich phase behavior of these systems has been found [13–17].

Reaction of α,ω -diamino terminated POP–POE–POP (Jeffamine ED-2003) with Bisphenol A propoxylate diglycidyl ether was used in preparation of elastic hydrophilic epoxy networks and hydrogels by Krakovský et al. [18–20]. Thermal properties of the hydrogels as well as aqueous solutions of Jeffamine ED-2003 were investigated by Gómez Ribelles et al. [21] and Salmerón-Sánchez [22]. It was demonstrated by Calvert [23] that epoxy curing can be also carried out directly in water environment to give hydrogels. In this way, epoxy-based hydrogels for sensor applications were prepared by reaction of Jeffamine ED-2003 with polyoxyethylene bis(glycidyl ether) in aqueous solution of sodium chloride [24].

In this work, epoxy networks were prepared by reaction of α,ω -diamino terminated POP's (Jeffamines, Series D) with polyoxyethylene bis(glycidyl ether) (POEBGE). The

aim of this study is an investigation of the effect of the molar mass of POP on thermal properties and swelling behavior of the epoxy networks and hydrogels prepared.

2. Experimental

2.1. Materials

The epoxy networks were prepared by the end-linking reaction of α,ω -diamino terminated polyoxypropylene (Jeffamine D-400, D-2000, and D-4000, Huntsman) of average molar mass 430, 2000, and 4000 g mol⁻¹ with polyoxyethylene bis(glycidyl ether) (Sigma–Aldrich) of average molar mass 526 g mol⁻¹. The chemical formulas of the reagents are depicted in Scheme 1. All the networks were stoichiometric ones, i.e., initial molar ratio of amino and epoxy groups (stoichiometric ratio), $r = 2[\text{NH}_2]_0/[\text{E}]_0 = 1.00$. The concentrations of amino groups in Jeffamines determined by titrations were $c_{\text{NH}_2} = 4.43 \times 10^{-3}$ mol g⁻¹ (D-400), 1.00×10^{-3} mol g⁻¹ (D-2000) and 0.453×10^{-3} mol g⁻¹ (D-4000), respectively. The concentration of epoxy groups in POEBGE determined by titration was $c_{\text{E}} = 3.86 \times 10^{-3}$ mol g⁻¹.

Both components were first stirred at 100 °C for about 15 min and then were poured into Teflon molds. The curing reaction of all systems proceeded at 120 °C for 48 h. The networks prepared were transparent. A small amount of extractable fraction – sol (2.8, 8.4 and 14.3 wt.%, see Table 2) remaining in the networks after curing process was removed by triple extraction in a good solvent (toluene). Finally, the networks were dried carefully, first in open air then in vacuum oven at 40 °C for 48 h.

Rectangular specimens were cut from the extracted and dry epoxy network and swollen to equilibrium in water at room temperature for 24 h to give rise to hydrogel samples.

2.2. Swelling behavior

First, the hydrogel samples were cooled down from room temperature to initial temperature (1 °C) and tempered for 24 h in a thermostated bath. Then, the samples were taken out of the water, quickly surface-dried, and weighed on an analytical balance. After mass determination the samples were immersed in water again, heated to a next temperature and tempered for 24 h again. The process was repeated until data at the highest temperature (90 °C) were obtained.

The mass fraction of polymer network in hydrogels, w_{netw} , is given by

$$w_{\text{netw}} = \frac{m_0}{m}$$

where m and m_0 are the masses of swollen and dry sample, respectively.

2.3. Dynamic mechanical analysis

Dynamic mechanical analysis was performed using a Seiko DMS210 Analyzer. Rectangular strips having dimensions ca 25 mm × 9 mm × 1 mm were cut from the sheets of the networks prepared. The strips were suspended between

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