

# Hydrophobic modification of high molar mass polyglycidol to thermosensitive polymers

M. Jamróz-Piegza, A. Utrata-Wesołek, B. Trzebicka, A. Dworak \*

*Institute of Coal Chemistry, Polish Academy of Sciences, PL-44-121 Gliwice, Poland*

Received 13 March 2006; received in revised form 26 April 2006; accepted 29 April 2006

Available online 21 June 2006

## Abstract

The results concerning a new class of thermosensitive polymers based on modified poly(2,3-epoxypropanol-1) – the polyglycidol are presented. Thermo-responsive water-soluble poly(glycidol-co-ethyl glycidyl carbamate)s were obtained by the hydrophobic modification of hydroxyl groups of the polyglycidol chain with ethyl isocyanate. The cloud points of the synthesized poly(glycidol-co-ethyl glycidyl carbamate)s were measured by UV–VIS and the hydrodynamic behaviour of the polymer chains near the transition temperature was characterized by dynamic light scattering. The influence of copolymer composition and polymer concentration on the cloud point was investigated. The cloud point was easily controlled in a range from 22 to 81 °C by change of the degree of modification. The effect of the surfactant sodium *n*-dodecylsulphate (SDS) and inorganic salt (NaCl) on the temperature response of synthesized copolymer was also examined.

© 2006 Elsevier Ltd. All rights reserved.

**Keywords:** Thermosensitive polymers; Polyethers; Polyglycidol; Hydrophobic modification; Cloud point; DLS

## 1. Introduction

Stimuli-sensitive polymers, known as “smart” or “stimuli-responsive”, are soluble or crosslinked polymers which show considerable and distinct, but reversible changes of physical and chemical properties in the response to stimuli of environment.

Such behaviour is observed for polymers in solution (mainly in water), macromolecules anchored on surface or for crosslinked polymers, like nano-particles or hydrogels [for reviews, see [1–4]]. Many

applications of stimuli-sensitive materials exist or are envisaged, including systems for controlled drug release and genes delivery vectors in medicine [5–7], bioseparation [8,9], development of new biocatalysts [10], biomimetic actuators [11], surfaces with switchable hydrophobic–hydrophilic properties and preparation of nano-devices and nano-reactors in micro- and nano-technology [12,13].

Temperature is the most widely used stimulus in environmentally sensitive polymers systems. Thermo-responsive polymers are soluble (water is the most investigated solvent) at low temperatures but precipitate when the solution is heated above a certain temperature, called the cloud point temperature ( $T_{CP}$ ) [3]. By plotting the cloud point temperatures

\* Corresponding author. Tel.: +48 32 2380780; fax: +48 32 2312831.

*E-mail address:* [adworak@karboch.gliwice.pl](mailto:adworak@karboch.gliwice.pl) (A. Dworak).

as a function of the polymer concentration the value of LCST (lower critical solution temperature) is obtained as the minimum of the curve [14].

For all applications the precise control of the phase separation temperature is of great importance. For the biomedical applications it is desired that the LCST value is placed near the physiological point, i.e. 37 °C. In the non-ionic polymers the value of this transition temperature is based upon the competition between the hydrophilic and the hydrophobic interactions. The control of the transition is possible, when a proper amount of properly distributed hydrophilic and hydrophobic elements are placed in the macromolecule.

Many polymers exhibit LCST: poly(*N*-substituted acrylamides) [15–17], derivatives of poly(vinyl alcohol) [18], poly(alkyl vinyl ethers) [19], poly(*N*-vinylcaprolactam) [20,21] or poly(2-ethyl-2-oxazoline) [22] are the most cited examples. It is also known that behaviour in water of some polyethers, such as poly(ethylene oxide) (PEO) [23], poly(propylene oxide) (PPO) [24] or poly(ethoxy ethyl glycidyl ether) (PEEGE) [25] exhibit phase separation above their lower critical solution temperatures. PEO exhibits relatively high LCST at 105 °C [23].

As the control of the transition point is essential and the chemical modification is the way of choice to achieve such control, many efforts have been spent on the chemical modification of the “basic” polymers to set the transition point to the desired value. The control of the  $T_{CP}$  value can be achieved by the copolymerisation with hydrophilic or hydrophobic moieties [16,26,27], modification of functional groups present in polymer chain [28,29] or by the addition of the salts or surfactants to the polymer solution [30,31].

Here we report the synthesis and behaviour in water of thermoresponsive poly(glycidol-co-ethyl glycidyl carbamate)s, a new class of thermosensitive polymers in which the thermal behaviour may easily be adjusted. The response of obtained systems to the temperature and the dependence of the cloud points on concentration, salt and of surfactant addition is described.

## 2. Experimental procedures

### 2.1. Materials

Ethoxy ethyl glycidyl ether (EEGE) was obtained by reacting 2,3-epoxypropanol-1 (glycidol) with

ethyl vinyl ether according to procedure described by Fitton et al. [32]. The obtained product was fractionated under reduced pressure. Fraction of purity exceeding 99.8% (GC) was used for polymerisation. Diethyl ether for polymerisation was refluxed over Na/K alloy. Diethyl zinc (1 M solution in hexane, Aldrich) and dibutyltin dilaurate 95% (DBTL) (Aldrich) were used as received. DMF (POCH Gliwice) was dried over  $\text{CaH}_2$ , distilled, then dried over  $\text{P}_2\text{O}_5$  and distilled again. Ethyl isocyanate 98% (Aldrich) was distilled under nitrogen atmosphere.

### 2.2. Polymerisation of ethoxy ethyl glycidyl ether

Ethoxy ethyl glycidyl ether was polymerised in bulk with  $\text{ZnEt}_2/\text{H}_2\text{O}$  (1:0.78) as catalyst using similar procedure as described by Spassky [33]. 1 M solution of diethyl zinc in hexane (35 mL) was added into the diethyl ether (35 mL) cooled to  $-10$  °C. Deionised water (0.027 mol, 0.493 mL) was slowly dropped during 4 h into this solution (1 droplet/2 min). The mixture was stirred for 24 h at room temperature. Next the solvents were evaporated and the EEGE (0.35 mol, 50 mL) was introduced. The molar ratio of diethyl zinc to monomer was 1:10. The polymerisation reaction was carried out for 24 h at 56 °C. Obtained poly(ethoxy ethyl glycidyl ether) was hydrolysed using 3 M HCl. The polymer solution was filtered and desalinated by dialysis against water. Water was evaporated and obtained polyglycidol was dried under reduced pressure.

### 2.3. Modification of polyglycidol

Polyglycidol was reacted with ethyl isocyanate in the presence of dibutyltin dilaurate as a catalyst, using DMF as the solvent. The concentration of polymer in solution was 15 g/L. The molar ratio of DBTL to OH groups was  $[\text{DBTL}]:[\text{OH}] = [0.01]:[1]$ . The amount of ethyl isocyanate varied from 0.06 to 0.40 mol per 1 mol of OH groups of polyglycidol units. The reaction was carried out at 40 °C for about 24 h. After the reaction the product was precipitated into diethyl ether cooled to  $-10$  °C and dried under reduced pressure.

### 2.4. Measurements

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of poly(glycidol-co-ethyl glycidyl carbamate)s were recorded in

Download English Version:

<https://daneshyari.com/en/article/1400263>

Download Persian Version:

<https://daneshyari.com/article/1400263>

[Daneshyari.com](https://daneshyari.com)