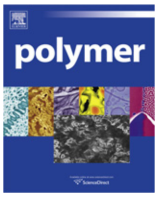
Polymer 52 (2011) 250–257

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



Synthesis and thermoresponsive properties of four arm, amphiphilic poly(*tert*-butyl-glycidylether)-block-polyglycidol stars

Marcin Libera [a], Barbara Trzebicka [a], Agnieszka Kowalczuk [a], Wojciech Wałach [a], Andrzej Dworak [a,b,*]

[a] *Centre of Polymer and Carbon Materials, Polish Academy of Sciences, M. Curie-Skłodowskiej 34, 41-819 Zabrze, Poland*
[b] *University of Opole, Institute of Chemistry, Oleska 48, 45-052 Opole, Poland*

ARTICLE INFO

Article history:
Received 16 August 2010
Received in revised form
26 October 2010
Accepted 2 December 2010
Available online 9 December 2010

Keywords:
Amphiphilic block stars
Thermosensitivity
Aggregation

ABSTRACT

A series of four arm stars with copolymer arms composed of poly(*tert*-butyl-glycidylether)-b-polyglycidol were prepared using a multi-step process based on anionic ring-opening polymerization. Control of the length of the arms and the number of functional (hydroxyl) reactive groups was achieved by anionic polymerization. Stars with molar masses up to 12200 g/mol were prepared. The amphiphilic character of the star structure was varied using different polyglycidol block lengths. The star structure and molar mass of the obtained stars were characterized by SEC–MALLS and NMR spectroscopy.

The temperature behavior of an aqueous solution of the obtained polymers was also investigated. The phase transition temperature was strongly dependent on the hydrophilic–hydrophobic balance of the star structure and varied in the range of 25–59 °C. As shown by DLS and SEM, the stars formed temperature-sensitive spherical aggregates in aqueous solution. The aggregates may be used for controlled transport and release of active compounds.

1. Introduction

Polymers with nonlinear topology have been extensively described in the literature [1–5]. Studies have focused on the synthesis, characterization and application of branched polymers.

Star polymers are macromolecules containing a single branch point from which arms spread out, forming macromolecules with a spherical architecture. The properties of star macromolecules are significantly different than those of linear chains of the same composition and molar mass. The preparation methods and properties of star polymers have been widely reviewed [2,6–10].

The classification of star polymers is frequently related to the structure of their arms. The simplest star structures contain chemically identical chains emanating from a central point. The arms of the stars may consist of the homopolymer chains (A_n type stars) or block copolymer $(AB)_n$ type stars. The stars consisting of chemically different arms are called miktoarm or heteroarm stars. Among all types of stars, symmetric and asymmetric stars are also distinguished. The asymmetric ones have arms of different molar mass, functional groups or topology.

There are two main synthetic methods used to obtain star polymers: “core-first” and “arm-first”. The “core-first” method is based upon the polymerization of a monomer, initiated by a polyfunctional core. The length of the star arms increases during polymerization. The “arm-first” method is based upon the synthesis of living macromolecular chains (the prospective arms of the star) and their termination with a multifunctional terminating agent, the core [8].

The number of initiation centers on the branch point of a star has to be higher than 2. The branch point can be composed of a multifunctional low molar mass compound [11–16], a dendrimer [17,18], a hyperbranched polymer [3,19–22], an arborescent structure [23,24] or a microgel [25,26]. When the core is big enough, the stars obtained are called core–shell structures. They exhibit interesting properties, especially when the internal and external parts are chemically different. The hydrophilic–hydrophobic balance between the core and shell may be controlled, when the arms of the star are generated using living polymerization techniques.

The formation of a micellar structure from star polymers in solvents with different selectivity for the blocks of star arms was reported [27–30]. The self-assembly of amphiphilic four arm stars with poly(ε-caprolactone)-block-poly(*N*-(2-hydroxypropyl)methacrylamide) arms in aqueous solution was investigated by Leroux [27]. The critical aggregation concentration and size of particles formed were measured as a function of copolymer composition and solution concentration. The micellization of four arm stars consisting of poly(acrylic acid)-b-polystyrene was reported by Monteiro [28].

---

* Corresponding author. Centre of Polymer and Carbon Materials, Polish Academy of Sciences, M. Curie-Skłodowskiej 34, 41-819 Zabrze, Poland. Tel.: +48 32 27 16 077; fax: +48 32 23 12 831.
E-mail address: adworak@cmpw-pan.edu.pl (A. Dworak).

0032-3861/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2010.12.001

The stars aggregated in water, forming core–shell micelles with sizes that increased with the length of the hydrophobic inner block. In DMF, a good solvent for both blocks no aggregation was observed. Micelle formation by other amphiphilic stars with poly(ethylene oxide)-b-poly(ε-caprolactone) or poly(ethylene oxide)-b-polylactide arms and PEO as an inner block were also presented [29]. Pispas et al. [30] reported the synthesis and micellization properties of eight arm polyisoprene-b-polystyrene stars that were prepared by anionic polymerization. The sizes and aggregation numbers of micelles depended on solvent selectivity.

The polymers of glycidol, which are hydrophilic polyethers that contain hydroxyl groups in their structures, have been intensively studied [31–35]. Polyglycidols with linear topology [31] and such of branched structures [32–35] were investigated. The anionic ring-opening polymerization of glycidol, with the use of slow monomer addition, leads to a branched polyether structure. Control of the molar mass and molecular structure of polyglycidol can be achieved by anionic polymerization of glycidol with a protected hydroxyl group [31–34].

Amphiphilic block copolymers, based upon glycidol and other oxiranes with different topologies, are investigated as new water soluble biocompatible materials [20,24,36–39]. The investigation uses highly branched copolymers of polyglycidol as biocompatible unimolecular micelles [20,24,36,37]. Linear copolymers of polyglycidol and other oxiranes that form micelles in water solutions were studied [38,39]. The relationship between the composition of the block copolymers and their association properties were investigated [39]. The modification of hydroxyl groups of polyglycidol to create amphiphilicity in this material was also investigated [38].

The precise synthesis of polyoxiranes with *tert*-butyl-glycidylether as a comonomer was reported recently [40,41]. The authors described the kinetics of the copolymerization of *tert*-butyl-glycidylether and allyl-glycidylether. The obtained copolymers were used to study the reaction condition for selective removal of the *tert*-butyl group [40]. The copolymer of *tert*-butyl-glycidylether and glycidol were used to functionalize hydroxyl groups with alkyl isocyanates [41].

Previous studies [24] of the copolymerization of ethylene oxide with 1-ethoxyethyl-glycidylether, and subsequent removal of 1-ethoxyethyl groups to recover the polyglycidol hydroxyl groups, has opened a route for preparing branched polyoxiranes with controllable molar masses and high hydroxyl group content.

Here we report the synthesis of four arm star block copolymers with well-defined amphiphilic arms of poly(*tert*-butyl-glycidylether)-block-polyglycidol with different polyglycidol block lengths. A multistep process, based on anionic ring-opening polymerization, was used for synthesis. The sensitivity of the star to temperature changes, accompanied by their aggregation behavior, is also described.

2. Experimental section

2.1. Materials

tert-Butyl-glycidylether (Aldrich) was dried for several days over CaH_2 and distilled before use. 1-Ethoxyethyl glycidylether was synthesized according to Fitton et al. [42], distilled several times under reduced pressure, stored over CaH_2 and distilled before polymerization. A fraction of 99.98% purity was used. Dimethyl sulfoxide (DMSO, POCh) was distilled over calcium hydride, stirred under argon with barium oxide for several days, and then distilled into an ampoule equipped with a Rotaflo glass–teflon valve. Tetrahydrofuran (THF,POCh) was dried over CaH_2, refluxed over Na/K alloy and distilled prior to use. Pentaerythritol (PENT, Aldrich) was crystallized from water and dried under high vacuum for several days. Potassium *tert*-butoxide (Fluka), formic acid and trichloroacetyl isocyanate (TCAI) were used as received.

Table 1
The molar ratios of monomers and yields of synthesis.

$S-[(BGE)_n-b-(EGE)_m]_4$			$S-[(BGE)_n-b-(G)_m]_4$		Ratio of blocks in arms[c]	
Monomer used [mol]			Conversion (%)[a]	Yield (%)[b]	Before hydrolysis	After hydrolysis
PENT	BGE	EGE			(BGE)/(EGE)	(BGE)/(G)
1.47×10^{-3}	0.058	0.041	99.9	88.3	1.38	1.44
1.61×10^{-3}	0.064	0.077	99.8	87.6	0.82	0.79
1.79×10^{-3}	0.079	0.108	99.9	89.2	0.72	0.69
1.22×10^{-3}	0.048	0.083	99.9	90.5	0.59	0.56
1.34×10^{-3}	0.053	0.113	99.8	87.7	0.47	0.45

[a] Measured by GC.
[b] Product after hydrolysis.
[c] Estimated after ^1H NMR analysis.

2.2. Synthesis of four arm [poly(tert-butyl-glycidylether)-block-polyglycidol]$_4$ stars $S-[(BGE)_n-b-(G)_m]_4$

2.2.1. Synthesis of potassium pentaerythritolate – initiator

Potassium alcoholate of pentaerythritol was prepared in DMSO. Dry pentaerythritol (1.47 mmol, 0.2 g) was placed in the reactor under argon atmosphere, additionally dried under a high vacuum, dissolved in DMSO (30 mL). All DMSO was removed under reduced pressure to remove adventitious water. The new portion of 30 mL of dry DMSO was added to the reactor along with the solution of potassium *tert*-butoxide (1.18 mmol, 0.13 g) in 20 mL DMSO. Nascent *tert*-butanol and almost all of the DMSO were removed by distillation under reduced pressure and the mixture was dissolved in 30 mL of dry DMSO. To avoid precipitation of the initiator from the solution, only up to 20% of all hydroxyl groups were ionized.

2.2.2. Synthesis of four arm [poly(tert-butyl-glycidylether)-block-poly(1-ethoxyethyl-glycidylether)]$_4$ stars $S-[(BGE)_n-b-(EGE)_m]_4$

All syntheses of star copolymers were carried out using a high-vacuum technique or dry argon atmosphere in reactors and ampoules equipped with glass–teflon valves. The proper molar ratios of the monomers used for star syntheses are placed in Table 1.

tert-Butyl-glycidylether (0.058 mol, 7.64 g) was distilled under high vacuum and placed in a reactor with a freshly prepared solution of potassium pentaerythritolate (partly ionized) (1.47 mmol) in 30 mL of DMSO. The reactor was placed in the oil bath and the mixture was stirred at 65 °C. After 24 h, freshly distilled THF (30 mL) was added to the reactor to keep the reaction mixture homogeneous. The polymerization was carried out at 74 °C. After 72 h, the conversion of *tert*-butyl-glycidylether was 100% (GC analysis). Freshly distilled 1-ethoxyethyl-glycidylether (0.041 mol, 5.99 g) was then added to the reactor. The reaction mixture was stirred at 74 °C for 72 h until complete conversion of the second monomer was achieved. The polymerization was terminated by adding water. After polymerization, the solvents were removed under reduced pressure, and the crude star block copolymer $S-[(BGE)_n-b-(EGE)_m]_4$ was analyzed by SEC–MALLS and ^1H NMR.

2.2.3. Deprotection of hydroxyl groups in the (EGE)$_m$ block

Each star $S-[(BGE)_n-b-(EGE)_m]_4$ (13.5 g) was dissolved in formic acid (30 mL). After dissolution, the formic acid was removed under reduced pressure and the remaining material was dissolved in 1,4-dioxane (100 mL). A solution of potassium hydroxide (6.5 g) in

$$C(CH_2OH)_4 + t\text{-}BuO^-K^+ \underset{\text{ionization}<20\%}{\overset{\text{DMSO}}{\rightleftharpoons}} (HOH_2C)_3C\text{-}CH_2O^-K^+ + t\text{-}BuOH$$

Scheme 1. The synthesis of potassium pentaerythritolate.