



Anionic ring-opening polymerization of ethylene oxide in DMF with cyclodextrin derivatives as new initiators

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ABSTRACT

Anionic polymerization initiated by cyclodextrins suffers from a poor solubility of those derivatives in standard polymerization solvents. The possibility to perform ethylene oxide polymerization initiated by monofunctional initiators (allyl alcohol, 2-methoxyethanol) by living ring opening polymerization in DMF, a good solvent for any CD derivative, was demonstrated by SEC, ¹H and ¹³C NMR analyses. The study was extended to the use of native CD as initiator, leading to the synthesis of ill-defined structures, explained by the reactivity scale of the various hydroxyl functions. Two selectively modified CD derivatives are then used to synthesize a new family of star-shaped poly(ethylene oxide) polymers with CD core, having 14 or 21 arms. The polymerization was found to be living and DOSY experiments confirmed the well-defined structures for the synthesized star-polymers.

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1. Introduction

Chemically modified cyclodextrins (CDs) allow numerous applications in several fields, such as drug delivery (Monnaert et al., 2004; Rajewski & Stella, 1996), catalysis (Badi et al., 2010), sensing (Ogoshi & Harada, 2008), and artificial channels (Bacri, Benkhaled, Guégan, & Auvray, 2005; Badi, Auvray, & Guégan, 2009; Jullien, Lazrak, Lacombe, Canceill, & Lehn, 1993; Tabushi, Kuroda, & Yokota, 1982). CDs offer the possibility to be selectively modified in order to synthesize new polymerization initiators. Various teams focused on the design of new CD-based initiators for the synthesis of star-shaped polymers using controlled polymerization (Yhaya, Gregory, & Stenzel, 2010). Seminal work was conducted by the group of Haddleton (Ohno, Wong, & Haddleton, 2001) and opened a new area in the design of star-shaped polymers by the use of modified CDs for ATRP polymerization. Styrene was successfully reported to be polymerized through this strategy, and various monomers such as (meth)acrylates, N-isopropylacrylamide were then used. In the mean time, Stenzel & Davis (2002) reported the synthesis of a heptafunctional trithiocarbonate β-CD derivative for controlled styrene polymerization by RAFT. Later on, Kakuchi et al. (2003) reported the synthesis of a TEMPO-modified β-cyclodextrin and

reported limitation of such strategy for the synthesis of well-defined star-shaped polystyrene with a cyclodextrin core. Anionic ring-opening polymerization with a CD-based initiator was first reported by Topchieva et al. (1998): by using native cyclodextrin as initiator of ethylene oxide polymerization, ill-defined polymers were synthesized. Harada and co-workers reported the polymerization of lactones (β-butyrolactone, δ-valerolactone, ε-caprolactone) initiated by native cyclodextrin. Surprisingly, only one arm per cyclodextrin was evidenced (Osaki, Takashima, Yamaguchi, & Harada, 2007). Gou, Zhu, Xu, and Shen (2008) noticed that the use of stannous octoate Sn(Oct)₂ allowed the initiation of all the primary hydroxyl functions for the polymerization of ε-caprolactone. Using β-butyrolactone, Harabagiu and co-workers observed that all the hydroxyl functions of the CD could participate to the polymerization reaction, despite a transfer reaction leading to linear polymer that was not discussed in the previous works (Peptu et al., 2010). Lactide and glycolide were also polymerized in bulk using native CD as initiator in the presence of Sn(Oct)₂ (Moogooe, Omid, & Davaran, 2010). Per-6-Tos-β-CD was synthesized by Adeli, Zarnegar, and Kabiri (2008) in order to initiate the polymerization of lactide using Sn(Oct)₂ as catalyst, then the tosylate functions of the CD primary face allowed the polymerization of 2-ethyl-2-oxazoline, through a cationic ring-opening polymerization (ROP). The ROP was also used by Pereira, Huin, Morariu, Bennevault-Celton, and Guégan (2012) to synthesize star poly(2-methyl-2-oxazoline) with 7 arms from β-cyclodextrin

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permodified on the primary rim, using the core-first and the arm-first methods.

Anionic polymerization of ethylene oxide has been extensively studied (Boileau, 1989; Lapienis & Penczek, 2004; Taton et al., 2003). Selectively modified β -cyclodextrin, by grafting heptyl chains on the secondary face (Badi et al., 2006), was used as initiator for ethylene oxide polymerization, and living nature of the polymerization in THF was proved (Badi et al., 2009). In a general concern, anionic polymerization initiated by cyclodextrins suffers from a poor solubility of those derivatives in standard polymerization solvents. This solubility matter prevents that field from a large development, like the design of well-defined nanopores (Badi et al., 2009). Thus, in this work, we investigate the possibility to perform ethylene oxide polymerization by living anionic ring opening polymerization, in DMF, a good solvent for any CD derivative. It was already demonstrated that, in the case of acrylonitrile (Jiang, Zhang, Du, Zhang, & Wang, 2007), the polymerization in DMF followed a living mechanism. The study is then extended to the use of native CD as initiator, the reactivity scale of the various hydroxyl functions being revisited. Various selectively modified CD derivatives are used to synthesize a new family of star-shaped poly(ethylene oxide) polymers with CD core, having 14 or 21 arms. The living mechanism of the polymerization is then demonstrated.

2. Materials and methods

2.1. Materials

DMF (SDS-Carlo-Erba) and DMSO (SDS-Carlo-Erba) were dried over CaH_2 using the freeze drying thaw technique and then distilled under vacuum, using the so-called “cold-wall” technique.

β -Cyclodextrin was kindly provided by Roquette (France). Per-(2,3,6-tri-*O*-methyl)- β -CD, per(2,3,6-tri-*O*-(3-hydroxypropyl))- β -CD and per(2,6-di-*O*-(3-hydroxypropyl)-3-*O*-methyl)- β -CD were synthesized as previously described (Badi et al., 2006; Casu, Reggiani, & Gallo, 1968; Eskandani, Huin, & Guégan, 2011). CD or CD derivatives were first introduced in a 100 mL burette surmounted with a stopcock, then dried under vacuum (10^{-5} mmHg) at room temperature for 12 h. Then, 10 mL of heptane distilled from CaH_2 were introduced in the burette by distillation. An azeotropic distillation of heptane/ H_2O was then conducted in order to eliminate the maximum of residual water from the CD (temperature of the azeotropic point: 79 °C). The same procedure was conducted using benzene. The CD initiator was then dried under high vacuum, 12 h, at 80 °C, and stored under vacuum.

2-Methoxyethanol (Aldrich) and allyl alcohol (Aldrich) were dried over molecular sieves (4 Å) for one night before being degassed and distilled in a 10 mL burette surmounted with a stopcock, and stored under vacuum.

Ethylene oxide (Aldrich) was dried on sodium films, until a pink color persisted, then the necessary amount of monomer was distilled in a 100 mL burette surmounted with a stopcock, and stored under vacuum.

The deprotonating agent, diphenylmethylpotassium (DPMK) in THF, was prepared as described previously (Normant & Angelo, 1960). Its concentration was determined by titration with acetanilide (Aldrich) in dried DMSO and was equal to 3.2×10^{-4} mol mL $^{-1}$. The required amount of DPMK was introduced in a 25 mL burette surmounted with a stopcock, and stored under vacuum.

2.2. Polymerization experiments

All vessels were flamed under high vacuum, prior to use. The solvent was vacuum-distilled in a 100 mL burette. Half of the

solvent was distilled in the burette containing the DPMK and the other half in the burette containing the initiator (CD derivatives or monoalcohol). The burettes were maintained under high vacuum. The reactor, a 250 mL four-neck flask equipped with a magnetic stirrer was surmounted with three burettes containing each the ethylene oxide, the solutions of initiator (cyclodextrin derivatives or monoalcohol) and DPMK both in DMF, and put under high vacuum (after flaming the reactor wall). All the polymerization reactions were carried out at 40 °C, under high vacuum. CD derivative (typically 0.390 g for a native CD in 40 mL of DMF) was first introduced, followed by the slow addition of DPMK (20% compared to the [OH], typically 3.43×10^{-4} mol in 35 mL of DMF). The obtained homogeneous solution was stirred during 48 h at room temperature. The reactive mixture was then cooled to 0 °C in order to add the ethylene oxide monomer (typically 14.4 g), in a dropwise manner. The polymerization was then carried out at 40 °C and the reaction was quenched by addition of acidic methanol. After concentration of the polymerization medium, the polymer was precipitated successively in cold diethyl ether and pentane.

2.3. Characterizations

NMR spectra were recorded on a Bruker Advance AM300 spectrometer (^1H 300 MHz and ^{13}C 75 MHz) using DMSO-d_6 as solvent at 25 °C. The molar masses were determined by size exclusion chromatography (SEC) with THF or DMF as eluents, the concentration of the polymer being 3 mg mL $^{-1}$. The column is a Styragel column (type HR 4E) from Waters. SEC was calibrated using poly(ethylene oxide) standards. The software used for the data analysis was OmniSEC (Viscotek). The molecular weights of the star polymers were then calculated considering the functionality of the initiator (Grest, Fetters, & Huang, 1997). The molar masses reported in the tables (NMR and SEC) stand for the purified star polymers (free from linear PEO).

Dynamic Light Scattering analysis was performed using a dynamic light scattering detector (Zetasizer nano ZS, ZEN 3500, Malvern) operating at a wavelength of 532 nm. Measurements were made at 25 °C at a scattering angle of 173°. Each measurement was repeated triplicate.

For the Diffusion-Ordered Spectroscopy (DOSY) experiments, the maximum field gradient strength was calibrated using a homemade Plexiglas phantom (8 mm \pm 0.01 length and a width equal to the inner diameter of the NMR tube) inserted in a H_2O filled NMR tube and using the pulse program calibgp (Bennevault-Celton et al., 2011; Seedhouse & Hoffman, 2008). The linear plot of the obtained gradient strengths against the gradient strength setting (GPZ1) used gave a maximum field gradient strength equal to 56.8 G cm $^{-1}$. The temperature calibration of the spectrometer was performed with a sample of 100% CH_3OH in the temperature range between 298 K and 313 K. The accuracy of the calibrations was checked by measuring the self-diffusion coefficient of a mixture $\text{H}_2\text{O}/\text{D}_2\text{O}$ (10%/90% in moles) at 25 °C (Holz & Weingärtner, 1991). The DOSY experiments were carried out using the step1s pulse sequence with a linear gradient of 16 steps between 2% and 95%. Before each diffusion experiment, the proton relaxation times were determined in order to correctly set the D1 parameter of the DOSY sequence. The length of the gradient δ and the diffusion time Δ were optimized for each analyzed product. All the DOSY experiments were carried out at 25 °C and the concentration used for each sample was equal to 16 mg mL $^{-1}$ in DMSO-d_6 . The mathematical treatment of the data was performed as previously described (Bennevault-Celton et al., 2011).

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