



The synthesis and characterization of multiarm star-shaped graft copolymers of polycaprolactone and hyperbranched polyester

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ABSTRACT

Simple and efficient method for the synthesis of multiarm star-shaped graft copolymers of polycaprolactone (PCL) and hyperbranched polyester Boltorn H40 (BH40) is presented. Grafting of ϵ -caprolactone (CL) from BH40 proceeds without the addition of a catalyst, and without drying of CL. *p*-Toluenesulfonic acid, which is added as a catalyst during the synthesis of BH40, acts also as a catalyst for CL grafting. Terminal –OH groups of BH40 react with CL, while the linear ones remain almost intact, except at high reactant ratio and prolonged reaction time. The presence of water changes the copolymer structure and properties, but the influence is minor. Star-shaped copolymers were prepared in a mass ratio of BH40:CL 1:1 to 1:10 and characterized. Glass transition temperature is decreasing while the degree of crystallinity is increasing with the increasing reactant ratio.

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1. Introduction

Polycaprolactone (PCL) is aliphatic, semicrystalline polyester with a broad spectrum of practical or potential applications. Although the PCL has been known for a long time it is gaining an increased scientific interest only in the last 10–15 years. PCL is not mechanically strong, yet it is miscible with many other polymers, which makes it suitable to tailor the mechanical and physical properties of polymers [1].

The main property of PCL, which makes it interesting, is its biodegradability. PCL is biodegradable by microbes [2] and enzymes [3] whereas it cannot be degraded enzymatically in the body [4]. Therefore, it can be used as implantable biomaterial, for drug delivery, as a scaffold for tissue repair etc. [5–7]. Biodegradability makes it especially interesting for food packaging. Various bio-based composites and nanocomposites have been prepared with starch, cellulose, nanocellulose and other natural fibres in order to improve mechanical properties without sacrificing biocompatibility and biodegradability [8,9].

In recent years there is an increasing interest in the synthesis of three, four, six and multi-arm star-shaped [10–15] and hyperbranched (HB) [16–19] polycaprolactone polymers and copolymers. Star polymers have better solubility, and lower viscosity, melting temperature, and degree of crystallization than their linear analogues. Multi-arm star-shaped PCL have been synthesized by grafting of ϵ -caprolactone from various HB polymers such as polyethylenimine [20], polyester urethane

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[21] and polyesters [22,23]. Potential application for those polymers are various, from epoxy toughener [24,25], PVC plasticizer [26], to various biomedical applications [6,11,15,27,28].

PCL and its block copolymers are typically prepared by ring-opening polymerization of ϵ -caprolactone (CL). Literature reports on various catalysts used for this purpose, i.e. various metal-based, enzymatic, organic amines and acids as well as inorganic acids. Many catalysts only work in the presence of initiator, which are mostly alcohol, amine or water [1]. Water can initiate but also terminate the polymerization reaction and therefore, CL and all other chemicals, usually have to be thoroughly dried.

This paper reports a simple synthesis and characterization of multi-arm PCL star shaped graft copolymer. Commercial, hydroxy-functional aliphatic hyperbranched polyester, synthesized from 2,2-bis(methylol)propionic acid (bis-MPA) Boltorn™ H40 (BH40), with 64 OH groups (theoretically), was used as a core molecule to which PCL was grafted. Multi-arm star-shaped polymers based on Boltorn™ hyperbranched polyesters have already been synthesized, but with a much higher reactant ratio (10–70) and different synthetic procedure as in the present article [22,23,28]. Those authors performed heavy drying of both HB polyester and ϵ -caprolactone, and added $\text{Sn}(\text{Oct})_2$ as a catalyst. Drying of CL by CaH_2 and distillation is needed from the scientific point of view, while it is economically hardly acceptable for industrial application, especially if the end-product is not used in medicine. On the other hand, there are several examples of CL polymerization and copolymerization in the presence of water, using 4-dimethylamino pyridine [29], metal triflates [30] or Brønsted acids [31].

Therefore, the goal of this research was to synthesize multi-arm graft copolymers hyperbranched polyester BH40-g-PCL without drying CL and to determine their properties. Contrary to other authors we were focused on the synthesis of multi-star copolymers with short PCL chains. Varying the chain length, one can vary the degree of crystallinity and crystallite size, which plays an important role in drug release behaviour [32].

2. Experimental section

Materials: Hyperbranched polyester Boltorn™ H40 is a product of Perstorp, Perstorp Sweden. Regular type of BH40 was used. ϵ -caprolactone (CL) and tetrahydrofuran were purchased at Aldrich. CL was kept in drybox (<0.1 ppm O_2 and <0.1 ppm H_2O) and used as received.

Characterization Techniques: ^1H NMR spectra were recorded in $\text{DMSO}-d_6$ solution at a concentration 10 mg/g on a Varian Unity Inova-300 spectrometer, both at room temperature and 75 °C. Differential scanning calorimetry (DSC) analysis was performed on a Mettler Toledo DSC-1 calorimeter. The samples were heated/cooled/heated in a temperature range –80 °C to 80 °C with heating and cooling rates of 10 K/min. All analyses were performed under a nitrogen atmosphere with a flow rate of 20 ml/min.

The determination of water content in CL: First, $\text{DMSO}-d_6$ was put in an NMR tube and the spectrum was recorded. The ratio of the water to $\text{DMSO}-d_6$ signal was calculated. Then, CL was added and spectrum was recorded. Filling of the NMR tube with both $\text{DMSO}-d_6$ and CL was performed in drybox to avoid air humidity entering the NMR tube. Both spectra were integrated and normalized to the same $\text{DMSO}-d_6$ signal strength. The difference in water signal intensity was compared to intensity of $-\text{CH}_2-\text{CO}-$ signal of CL to calculate molar% of water.

Molar masses were determined by size exclusion chromatography (SEC) combined with multiangle light scattering (MALS) and RI detector. Columns $\mu\text{Styragel HR5E}$, 5 μm (Polymer Laboratories) and Mesopore, 3 μm (Polymer Laboratories) were used. The nominal eluent (THF) flow rate was 0.8 mL min^{-1} . The mass of the samples injected into the column was typically 1.0×10^{-3} g, whereas the solution concentration was 0.01 g/mL^{-1} . All the samples were filtered through 0.45 μm PTFE filter.

2.1. Grafting of PCL from BH40

Grafting of PCL from BH40 was performed in bulk. 2.0–5.0 g of BH40 was put in a weighted two-necked round bottom flask (100 ml) equipped with the magnetic stirrer, water condenser and rubber septum. The content of the flask was purged with nitrogen through the injection needle stabbed into rubber septum, stirred and heated to 145 °C to melt BH40 and to break strong H-bonds, which develops on time [33]. Then, the purging was stopped, and CL was injected through the rubber septum. A weight ratio of BH40 to CL, which corresponds to molar ratio of $-\text{OH}$ groups to CL, was from 1:1 (BH40g1) to 1:10 (BH40g10). After 2.5 h, nitrogen purging was applied again for 30 min in order to remove drops of CL and/or water condensed on the flask wall. After that the flask was lifted from the oil bath, cooled to room temperature and weighted. Immediately, NMR spectra were recorded in order to determine the presence of unreacted CL and to calculate the conversion. Unreacted CL was only observed in samples prepared with reactant ratio 1:4 and higher. Reaction time for those samples was prolonged to 5, 10 or 24 h.

3. Results and discussion

The products of BH40 and CL polymerization were transparent viscous liquids. BH40g10 and BH40g5 crystallized on cooling to room temperature, while all others remained transparent. It was only after a few ours or weeks that the turbidity appeared, indicating a slow crystallization, which turned them into white solids within 2–3 months. All copolymers were soluble in nonpolar solvents like toluene and chloroform and in polar solvents like DMSO and acetone. They were also

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