Available online at www.sciencedirect.com
ScienceDirect
European Polymer Journal 44 (2008) 1060–1070
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

Core-shell type multiarm star poly(ε-caprolactone) with high molecular weight hyperbranched polyethylenimine as core: Synthesis, characterization and encapsulation properties

Xulong Cao [a], Zhenquan Li [a], Xinwang Song [a], Xiaohong Cui [a], Pengfei Cao [b], Huaji Liu [b], Fa Cheng [b], Yu Chen [b,*]

[a] *Geological Scientific Research Institute of Shengli Oilfield, Dongying 257015, Shandong Province, People's Republic of China*
[b] *Department of Chemistry, School of Sciences, Tianjin University, Tianjin 300072, People's Republic of China*

Received 15 December 2007; received in revised form 22 January 2008; accepted 24 January 2008
Available online 2 February 2008

Abstract

Core-shell type multiarm star copolymers with poly(ε-caprolactone) (PCL) as shells and hyperbranched polyethylenimine (PEI) as core have been successfully prepared by the $Sn(Oct)_2$ catalyzed ring-opening polymerization of ε-caprolactone (CL) using high molecular weigh PEIs directly as macroinitiators. The initiation efficiency is in the range of 91–95% for PEI with $M_n = 10^4$ (PEI10K) and only around 60% for PEI with $M_n = 2.5 \times 10^4$ (PEI25K), leading to star polymers with an average arm number in the range of 155–276. The thermal property of the obtained multiarm star polymers were also investigated by DSC. The melting and crystallization temperatures of the star polymers increase as the PCL arm length increases when the PEI core is fixed. The fusion enthalpy, crystalline enthalpy and degree of crystallinity values of the star polymers with PEI10K core are less than those with PEI1.8K core. Due to the polarity difference between PCL arm and PEI core, the resulting multiarm star polymers can act as inverted micellar nanocapsules capable of extracting and encapsulating water soluble guests. Increasing the size and polarity of the hydrophilic PEI core of the star nanocapsules are two effective ways to enhance their hydrophilic guest encapsulation capacity. Increasing the hydrophobic PCL arm length can increase the molar ratio, whereas reduce the weight ratio of the encapsulated hydrophilic guests to the star nanocapsules. Unexpectedly, the obtained nanocapsules can entrap the bigger size hydrophilic congo red guests more than the smaller size methyl orange.

Keywords: Hyperbranched; Polyethylenimine; ε-Caprolactone; Star polymer; Inverted micelle; Encapsulation

1. Introduction

Multiarm star polymers have recently attracted considerable attention due to their unusual bulk and solution properties [1,2]. Two major strategies have been employed for their preparation: (i) the *core-first* approach consisting of living polymerization on the basis of a multifunctional initiator-core; (ii) the arm-first approach, which consists of the quenching of living polymers with a multifunctional coupling agent or linking reactions of living polymers with a small amount of bifunctional vinyl

* Corresponding author. Tel.: +86 22 27405053; fax: +86 22 27403475.
E-mail address: chenyu@tju.edu.cn (Y. Chen).

0014-3057/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2008.01.035

compounds. Among these two strategies, polymerization with a multifunctional initiator and quenching of living polymers with a multifunctional coupling agent lead to star polymers with predetermined numbers of arms, however, linking reactions of living polymers with a small amount of bifunctional vinyl compounds afford star polymers with a random distribution of arms per polymer.

Dendrimers [3–8], hyperbranched polymers [9–15] and cyclodextrins [16–18] are attractive compounds as macroinitiators for the preparation of multiarm star polymers using the core-first strategy. Cyclodextrins are similar to dendrimers, having well-defined structure and exact functionality. However, cyclodextrin species are scarce, limited to α, β, γ-cyclodextrin with 18, 21 and 24 hydroxyl groups, respectively. In addition, though dendrimers and hyperbranched polymers with functionalities more than 100 are available; the number of multiarm star polymers obtained by the core-first strategy involving such multifunctional materials is very limited [14]. Yet, the star polymers with arm numbers more than 100 are usually prepared through the arm-first strategy [19–21].

Until now, a limited number of hyperbranched polyols have been employed as core for the syntheses of multiarm star poly(ε-caprolactone) (PCL), such as hyperbranched polyglycerol [15], hyperbranched poly(3-ethyl-3-hydroxymethyl oxetane) [22] and hyperbranched polyester polyols [14]. The respective polarity of the hyperbranched core and the PCL arm is similar, thus, the obtained star polymers do not exhibit the expected core-shell structures required for the encapsulation of guest molecules. Unfortunately, the hyperbranched polymer backbones were only used as support for the PCL arms and no further applications derived from their presence was discovered. Furthermore, the PCL arm numbers of all the obtained star polymers are less than 100 due to the limited functionality number of the employed hyperbranched polyols.

Commercially available hyperbranched polyethylenimine (PEI) is a well-known functional polymer and its application fields are very wide. For example, PEI has been used for a long time not only for various industrial purposes, e.g., as flocculating agents, thickeners and dispersion stabilizers, but also in biomedicine application, such as gene transfer processes [23–25]. Furthermore, PEIs modified with aliphatic chain through amide or ketone linkage have been addressed as unimolecular inverted micelles for efficient anionic dye encapsulation due to their compact core-shell structures [26–29]. Recently, PEI with $M_n = 1800$ (PEI1.8K) was reported to initiate the ring-opening polymerization of CL with almost ca. 100% initiating efficiency, resulting in average 30 arm star polymers with PEI as core and PCL as arms [10]. The obtained multiarm star polymers could encapsulate water soluble dye; however, the encapsulation efficiency was very low. Subsequently PEI with $M_n = 10{,}000$ (PEI10K) was addressed by Adeli et al. as macroinitiator for the ring-opening polymerization of lactide, resulting in multiarm star polymers with PEI as core and polylactide as arms [30], however, according to their data the initiating efficiency was only found to be of 40%, implying that the arm numbers of the obtained star polymers were only around 70. It has been known that the higher the generation of dendrimer is, the more crowed the terminal groups on the periphery of dendrimer are [31,32], which is also the case for their imperfect hyperbranched analogues [33]. Thus, the lower initiation efficiency of PEI10K for the ring-opening polymerization of lactide may be attributed to the steric hindrance of the crowded terminal primary and secondary amines of PEI10K.

Herein, we report the ring-opening polymerization of CL initiated by high molecular weight PEIs, leading to core-shell type star block copolymers polyethylenimine-*block*-poly(ε-caprolactone) (PEI-*b*-PCL) with an average arm number in the range of 155–276. The resultant polymers can efficiently encapsulate hydrophilic guest molecules. Since the commercially available PEIs have been widely used in gene transfer processes [23–25], and PCL is also a well-known biocompatible polymers, the obtained amphiphilic multiarm star copolymers are promising composites with respect to biomedical applications.

2. Experimental

2.1. Materials

Hyperbranched polyethylenimines, PEI1.8K (Polysciences, $M_n = 1800$ g/mol, $M_w/M_n = 1.04$), PEI10K (Aldrich, $M_n = 10^4$ g/mol, $M_w/M_n = 2.5$) and PEI25K (Hyperpolymers GmbH, $M_n = 2.5 \times 10^4$ g/mol, $M_w/M_n = 2.5$) were dried under vacuum prior to use. ε-Caprolactone (CL, 99%, Acros) was distilled from CaH_2 under reduced pressure. Tin(II) 2-ethylhexanoate ($Sn(Oct)_2$, 97%) was purchased from Alfa Aesar and used directly. methyl orange (MO, >85%) was purchased from