4개의 폴리카프로락톤 가지 코어를 가지는 스타형 폴리카프로락톤의 합성 및 분석

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Synthesis and characterization of Star Shape Polycaprolactone containing 4-Arm Polycaprolactone Core

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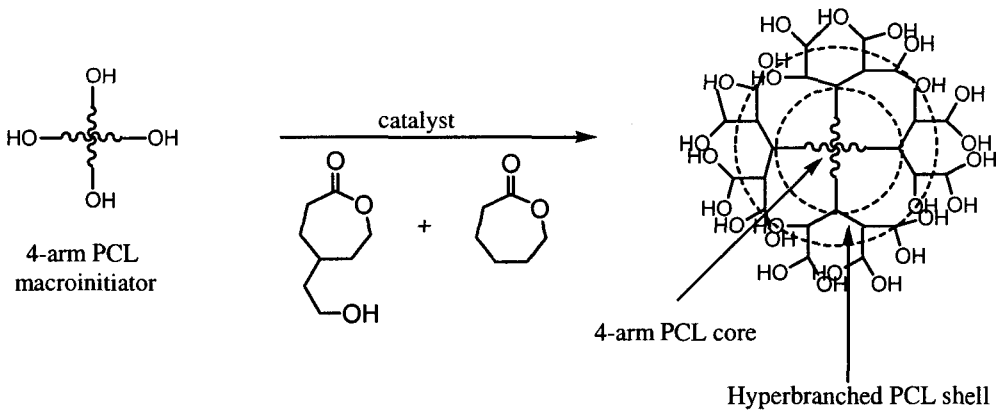
INTRODUCTION

The synthesis of materials with controlled composition and architectures continues to be a focus of considerable current research. Dendritic multiarm polymers such as dendrimer, hyperbranched polymer, and star polymers are three dimensional macromolecules, in which a large number of linear arms of similar molecular weight and narrow molecular weight distribution emanate from a central core. This class of star polymers recently attracts increasing interest due to the compact structure, their end functionalities, and the lower viscosities than linear analogs of similar molecular weight[1]. Dendrimers require multistep synthesis and purification. Hyperbranched polymers were synthesized by one-pot synthesis of AB_2 type monomers. Recently synthesis of these materials is expanded to AB^* type monomers so called self-condensing polymerization[2]. Well-defined star polymers are typically prepared by various living polymerization techniques. There are three basic synthetic routes for star polymers. The core first technique[3] involves the use of a multifunctional initiator, and the number of arms in star polymer can be determined by the number of initiating sites on the initiator. The arm first technique[4] involves the synthesis of preformed arms, usually through living polymerization, followed by the reaction with a multifunctional linking agent. The third method[5] is a slight variation of the arm first technique. which sometimes is also termed the nodule method. In this method, the reactive macroinitiators (arms) produced by a living polymerization technique are cross-linked by divinyl compounds to form star polymers.

Aliphatic polyesters such as poly(ε-caprolactone) (PCL), poly(D- or L-lactide)

etc. were intensively studied in bio-application areas of polymers due to their biocompatibility and biodegradability. General types of these polymers in bioactive materials are amphiphilic block, graft type copolymers. But control of physical properties such as biodegradability etc. of linear PCL is difficult because these polymers were semi-crystalline and hydrophobic. Recently, to control crystallinity many research groups introduced the modified polymer structures such as branched structure or hydrophilic groups. For example, J. L. Hedrick[6] et al. synthesized star and hyperbranched PCLs and PCLs containing functional groups such as amine, carbonyl, hydroxy groups. H. Frey[7] et al. synthesized hyperbranched polyester using 2,2-(bishydroxymethyl)propionic acid as AB_2 type monomer. M. J. Fréchet[8] et al. synthesized hyperbranched PCL using 4-(2-hydroxyethyl)-ε-caprolactone (HECL) as AB type monomer. The physical properties such as mechanical, rheological, and solution properties of these polymers depend on the type and degree of branching.

In this study, we report the synthesis of dendritic polycaprolactone containing 4-arm PCL core and branched PCL shells.



Scheme 1. Synthesis of Star Shape Polycaprolactone

EXPRIMENTAL

Synthesis of 4-(2-Hydroxyethyl)-ε-caprolactone[8]

4-(2-Hydroxyethyl)-ε-caprolactone was synthesized according to a literature procedure.

Synthesis of 4-arm PCL macroinitiator

Caprolactone, tin octoate, pentaerythritol were transfered to flame dried round bottom flask via cannular. N_2 gas was bubbled for 15 minute. Polymerization

proceeded in thermostated oil-bath at 70 ℃. The polymerization solution was diluted by adding toluene and then precipitated in hexane. The obtained polymer was dried in vacuum oven and characterized.

General polymerization procedure

HECL, caprolactone, 4-arm PCL macroinitiator, tin octoate were added to nitrogen filled round bottom flask. Other procedures are proceded by a similar approach as describe above.

Characterization

^{1}H and ^{13}C NMR spectra were recorded with a Varian Gemini 300 MHz spectrometer. Gel Permeation Chromatography (GPC) was carried out on a Waters chromatography connected to a Waters 410 differential refractometer, using polystyrene of known molecular weight as the calibration standard.

RESULT AND DISCUSSION

The synthetic route of star-shape polycaprolactone is shown in the scheme 1. 4-Arm PCL macroinitiator was synthesized by ring opening polymerization of caprolactone using pentaerythritol as initiator and tin octoate as catalyst. HECL was synthesized according to a literature procedure. Star shape amphiphilic block copolymers were synthesized by bulk polymerization at 70 ℃. In case of AB^{*} type monomer polymerization is proceeded according to self-condensing polymerization and these monomers produced hyperbranched polymers having relatively high chain density. In order to control chain density we copolymerized HECL and caprolactone with various molar ratio. The synthesized polymer has core-shell structure and hydroxy functional groups in its chain end. The physical properties such as solubility and crystallinity etc. of polymer is turnable according to mole ratio of caprolactone, HECL, 4-arm macroinitiator. The chain density of polymers can be controlled by the mole ration of caprolactone and HECL. The GPC chloromatograms of star-shape polycaprolactone is shown in figure 1. The peak molecular weight (Mp) of synthesized polymer was increased to 22600 dalton from 12500 dalton. From this result, we known the star shape PCL was synthesized. But small amount of linear oligomeric PCL initiated by HECL is also shown.

CONCLUSION

We synthesized new star-shape PCL using 4-arm initiator as a core and AB^{*} type 4-(2-hydroxyethyl)-ε-caprolactone monomer as a arms. The resulting polymers have biodegradable aliphatic ester groups, relatively high chain end

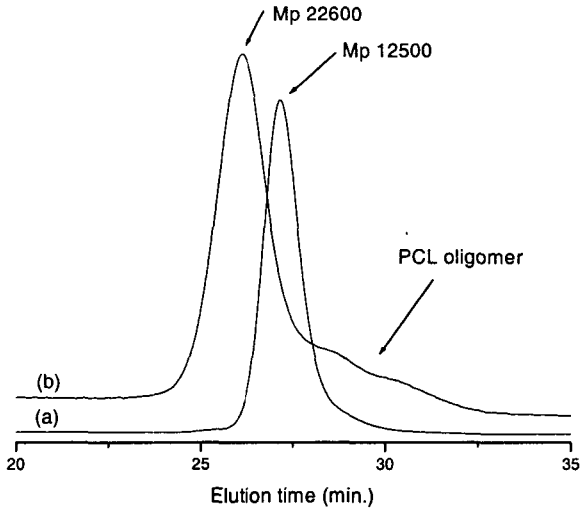


Fig. 1. GPC chromatograms of synthesized star PCL (b) and 4-arm PCL macroinitiator (a). $[CL]_0$ = 37.9 mol/L, [4-arm PCL] = 0.1 mol/L, [HECL] = 2 mol/L, [tin octoate] = 0.02 mol/L, Temp. = 70℃, time = 18 h, 4-arm macroinitiator Mn = 11, 000 g/mol, PDI = 1.10

functionality, and highly branched structures. Thus these materials are expected to be bioactive materials and have different physical properties compare with their linear analogs. The detailed structural characterization and physical properties of these new star-shape PCLs are currently under investigation

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