

Synthesis and Characterization of Amphiphilic Dendron based Triblock Copolymers

Byoung-Ki Cho*

Department of Chemistry, Institute of Nanosensor and Biotechnology, Dankook University, Seoul 140-714, Korea

ABSTRACT

A novel triblock copolymer consisting of an amphiphilic 4th generation aliphatic polyether dendron, hydrophilic poly (ethylene oxide), and hydrophobic amorphous polyisoprene was prepared. The synthesis of the monodisperse triblock copolymer with the well-defined polymeric architecture was achieved using a combination technique composed of anionic polymerization of poly (ethylene oxide)-*block*-polyisoprene (PI-*b*-PEO), a stepwise convergent synthetic method of the amphiphilic dendron, and an efficient coupling reaction of the former two precursors. The triblock copolymer has a number average molecular weight of about 11,000 g/mol, and shows a very narrow polydispersity (M_w/M_n) of less than 1.05, indicative of the well-defined chain structure. The thermal analysis demonstrates that each block is well microphase-separated and the hydrophilic PEO coils are plasticized by the dendritic cores in the solid state.

Key words : triblock copolymers, dendron, esterification coupling reaction.

Introduction

To tailor well-defined polymeric structure is of great importance in soft materials with respect to the manipulation of physical properties in the bulk and solution. Recently, this issue moves rapidly toward the creation of organized nano-structures which have tremendous potentials for novel functionalities (1). Until now, to pursue this goal, many groups have adopted the simplest polymeric system, i.e. linear type block copolymers, and deeply investigated their self-assembled nanostructures because of the synthetic convenience (2).

Dendrimers/dendrons are regularly branched macromolecules which have received a great amount of attention due to their unique structural and physical uniqueness (3). Recently, these macromolecules have been integrated with

architecturally distinct linear type block copolymers into a novel class of polymeric hybrids (4). More recently, introduction of microphase-separation concept to the hybrid architecture has been proved to lead to a self-assembling system which shares the morphological behavior of dendrimer/dendrons and linear block copolymers (5). However, this dendron and linear polymer fused system has not been extended to more complicated chain architectures, for representative example, triblock copolymers. Therefore, it can be an interesting challenge to synthesize a dendron based triblock copolymer. To this end, I have designed and synthesized a novel triblock copolymer which consists of a hydrophobic crystalline peripheries (docosyl chains), a hydrophilic part [dendritic core plus poly (ethylene oxide) (PEO)], and a hydrophobic amorphous coil [polyisoprene (PI)].

Herein, the present article mainly describes a synthetic route to the dendron based triblock copolymer by a combination of anionic polymerization, a convergent dendron synthetic method, and an esterification coupling reaction. Also,

* Corresponding author :
 Byoung-Ki Cho
 Tel : +82-2-799-1397
 Fax : +82-2-792-9269
 E-mail : chobk@dankook.ac.kr

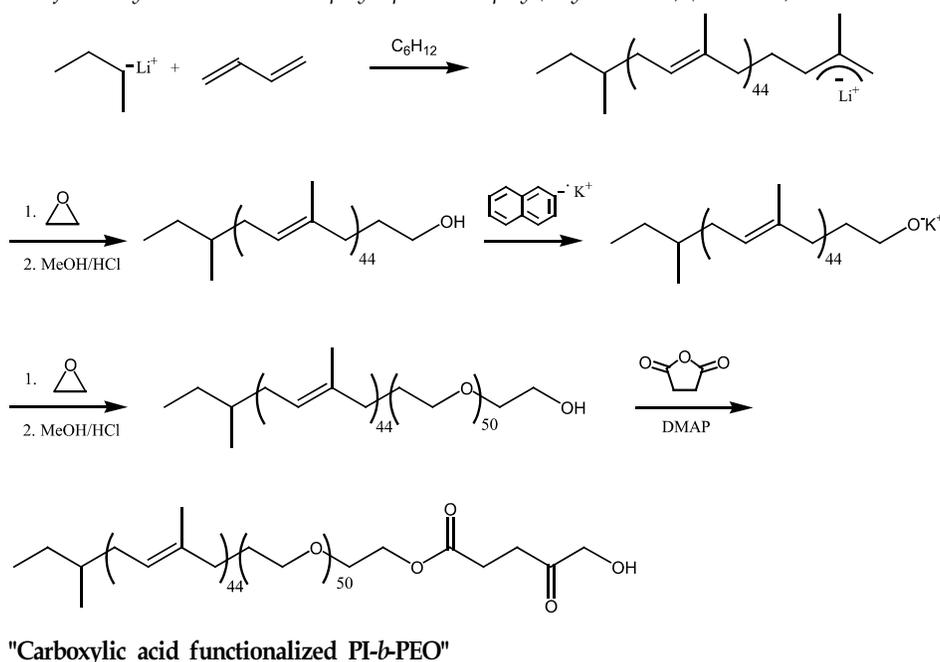
the thermal behavior of the polymer is discussed.

Results and Discussion

The synthesis of PI-*b*-PEO was performed via a stepwise process described in **Scheme 1** (6). In the first step isoprene was polymerized in cyclohexane with *sec*-butyllithium as an initiator. To convert the living PI end into hydroxy group,

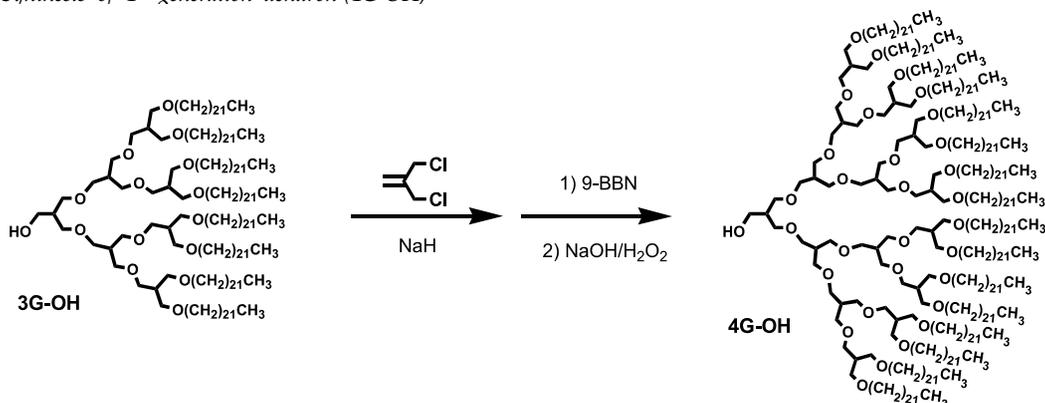
ethylene oxide was added and then subsequently oxanion of the resulting PI chain was protonated with degassed methanolic HCl. In the next step potassium naphthalenide was used to remove the proton on the hydroxyl group resulting in PI-OK⁺. Polymerization of ethylene oxide at the end of PI was performed in tetrahydrofuran in the presence of a five-fold excess of KCl with respect to PI-OH chain ends. The polymerization was terminated with degassed methanolic HCl, yielding hydroxy group ended

Synthesis of carboxylic acid terminated polyisopren-block-poly (ethylene oxide) (PI-b-PEO)



Scheme 1. Synthesis of carboxylic acid functionalized PI-*b*-PEO.

Synthesis of 4th generation dendron (4G-OH)



Scheme 2. Synthesis of 4G-OH.

PI-*b*-PEO. Then, the PI-*b*-PEO was functionalized with carboxylic acid by the reaction with succinic anhydride in the presence of 4-dimethylaminopyridine (DMAP). The structural analysis from GPC and NMR determines that the molecular weights of PEO and PI are 2170 and 3000 g/mol, respectively (7).

The synthesis of 4G-OH was performed using the convergent synthetic method (**Scheme 2**). Basically, the synthetic scheme consists of two major organic reactions such as a Williamson etherification (*generation growth step*) and hydroboration/oxidation (*activation step*) reactions (8). In the generation growth step, a precursor molecule, i.e. 3th generation dendron (3G-OH), was reacted with methylalyl dichloride in the presence of sodium hydride in THF and DMF solvent mixture. Then, in the activation step, the resulting olefin group of the 4th generation dendron was converted into hydroxy group via hydroboration (using 9-BBN) and oxidation ($\text{H}_2\text{O}_2/\text{NaOH}$) reactions. The 4G-OH was characterized by NMR, GPC, Mass spectrometry (7). Polydispersity value from GPC was determined to be 1.02, indicative of the high purity (**Fig 1**). This result is in good agreement with the single molecular ion peak in the mass spectrum (data not shown).

The final triblock block copolymer was prepared through a simple condensation reaction using *N,N'*-diisopropylcarbodiimide (DIPC) and 4-(dimethylamino)pyridinium-*p*-toluene sulfonate (DPTS) (**Scheme 3**). The ester linkage can be formed

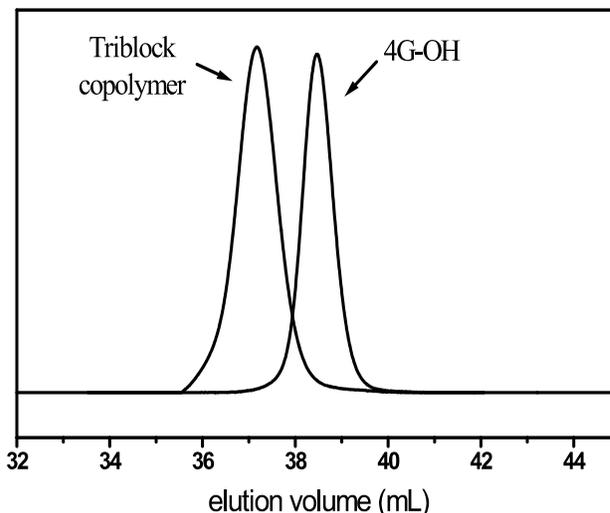
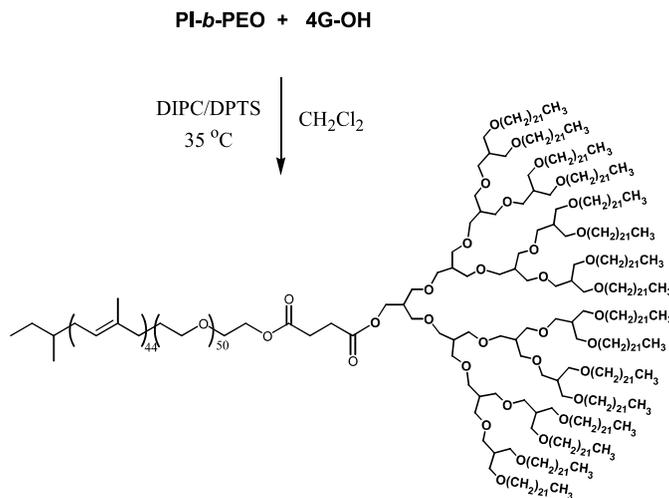


Fig 1. GPC elugrams of 4G-OH and the triblock copolymer.

by the coupling reaction of carboxylic acid of PI-*b*-PEO with hydroxy group of 4G-OH (7). In this reaction, a two fold excess of 4G-OH with respect to PI-*b*-PEO was used to obtain high yield and purification convenience. The final triblock copolymer was yielded quantitatively (yield after purification > 90%). The molecular weight and polydispersity were characterized by GPC and mass spectrometry. The number average molecular weights (M_n) from both techniques are estimated to be about 11,000 g/mol (11100 and 10320 g/mol estimated from GPC and mass spectrometry) which are nearly consistent with the value (11446 g/mol) from the summation

Synthesis and thermal properties of triblock copolymer



Scheme 3. Synthesis of triblock copolymer.

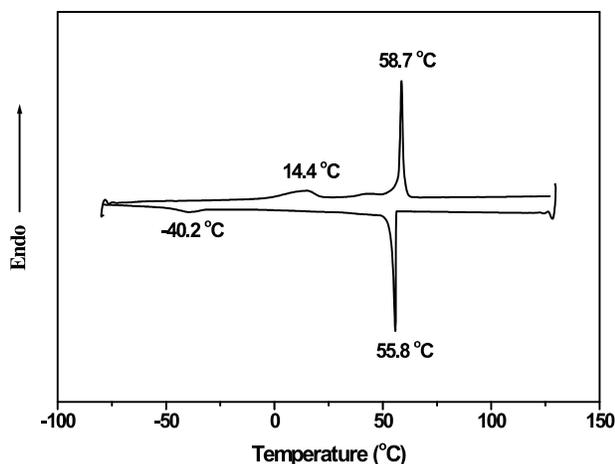


Fig 2. DSC thermograms of (a) heating scan on the upper and (b) cooling scan on the lower of the triblock copolymer. The first and second first order transitions correspond to the PEO and docosyl group melting transitions, respectively.

of individual M.W.s of PI-*b*-PEO and 4G-OH. The polydispersities from GPC and mass spectrometry show narrow values (determined as 1.05 and 1.02), confirming that the triblock copolymer has the well-defined chain architecture (**Fig 2**).

As mentioned earlier in the introduction section, the triblock copolymer has three different blocks which are the hydrophobic crystalline docosyl peripheries, hydrophilic part (dendritic core plus PEO), and hydrophobic amorphous PI. Three blocks are expected to show the different thermal behavior in the solid state due to their distinct segmental structures, which was characterized by differential scanning calorimetry (DSC). On both heating and cooling scans, two peaks are observed, corresponding to the melting transitions of docosyl peripheries and PEO, respectively. Compared to the docosyl peripheries melting temperature of 4G-OH (61°C), the docosyl melting temperature of the triblock copolymer (59°C) is almost comparable. This indicates that the other hydrophobic amorphous PI is not mixed with docosyl peripheries in the solid state, thus all three blocks are microphase-separated. More remarkably, the PEO melting transition temperature is significantly suppressed in comparison with that (52°C) of homo-PEO with the similar M.W. of 2,000 g/mol. This is strongly suggesting that PEO chains are plasticized by the amorphous hydrophilic dendritic core because

of the similarity in chemical composition (9).

Conclusion

A combination synthetic strategy of anionic polymerization, a stepwise convergent dendron synthetic method, and an esterification coupling reaction, proved to be an effective route for the formation of a novel nanoscopic triblock copolymer consisting of [1] hydrophobic crystalline peripheries as a hydrophobic crystalline block, [2] a dendritic core plus poly(ethylene oxide) coil as a hydrophilic block, and [3] polyisoprene as a hydrophobic amorphous block. The triblock copolymer has molecular weight (M_n) of about 11,000 g/mol, and shows very narrow molecular weight distributions (less than 1.05 from both GPC and mass spectrometry) indicative of well-defined chain structure. Differential scanning calorimetry analysis suggests that the three blocks are microphase-separated in the solid state.

References

- (1) Förster S, Konrad M (2003) *J. Mater. Chem.* **13**, 2671.
- (2) Hillmyer MA, Bates FS, Almdal K, Mortensen K, Ryan AJ, Fairclough JPA (1996) *Science* **271**, 976.
- (3) Bosman AW, Janssen HM, Meijer EW (1999) *Chem. Rev.* **99**, 1665.
- (4) Gitsov I, Fréchet JM (1996) *J. Am. Chem. Soc.* **118**, 3785.
- (5) Cho B-K, Jain A, Gruner SM, Wiesner U (2004) *Science* **305**, 1598.
- (6) Templin M, Franck A, Du Chesne A, Leist H, Zhang Y, Ulrich R, Schadler V, Wiesner U (1997) *Science* **278**, 1795.
- (7) **Carboxylic acid functionalized PI-*b*-PEO:** ^1H NMR (CDCl_3 , δ , ppm): 5.0-5.25 (m, $\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2$), 4.6-4.8 (m, $\text{CH}_2\text{CH}(\text{CH}_3)=\text{CH}_2$), 4.23 (t, $\text{CH}_2\text{OCO}(\text{CH}_2)_2\text{COOH}$, $J = 4.5$ Hz), 3.30-3.90 (m, $\text{CH}_2\text{CH}_2\text{O}$), 2.62 (m, $\text{CO}(\text{CH}_2)_2\text{COOH}$), 0.8-2.2 (m, $\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2$ and $\text{CH}_3\text{CH}_2\text{CHCH}_3$); **4G-OH:** ^1H NMR (CDCl_3 , δ , ppm): 3.72 (d, CH_2OH , $J = 5.0$ Hz), 2.98-3.62 (m, $\text{OCH}_2\text{CH}(\text{CH}_2\text{O})_2$ and $\text{OCH}_2(\text{CH}_2)_{20}$), 2.13 (m, $\text{OCH}_2\text{CH}(\text{CH}_2\text{O})_2$), 0.80-1.65 (m, $\text{OCH}_2(\text{CH}_2)_{20}\text{CH}_3$);

Triblock copolymer. ^1H NMR (CDCl_3 , δ , ppm): 5.0-5.25 (m, $\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2$), 4.6-4.8 (m, $\text{CH}_2\text{CHC}(\text{CH}_3)=\text{CH}_2$), 4.23 (t, $\text{CH}_2\text{OCO}(\text{CH}_2)_2\text{COOH}$, $J = 4.5$ Hz), 4.15 (d, CH_2OOC , $J = 5.0$ Hz), 3.0-3.95 (m, $\text{CH}_2\text{CH}_2\text{O}$, $\text{OCH}_2\text{CH}(\text{CH}_2\text{O})_2$ and $\text{OCH}_2(\text{CH}_2)_{20}$), 2.62 (m, $\text{CO}(\text{CH}_2)_2\text{CO}$), 0.8-2.2 (m, $\text{OCH}_2(\text{CH}_2)_{20}\text{CH}_3$, $\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2$ and $\text{CH}_3\text{CH}_2\text{CHCH}_3$).

(8) Jayaraman M, Fréchet JMJ (1998) *J. Am. Chem. Soc.* **120**, 12996.

(9) Gitsov I, Wooley KL, Hawker CJ, Ivanova PT, Fréchet JMJ (1993) *Macromolecules* **26**, 5621.

(Received May 4, 2005; Accepted Jul 15, 2005)