

Synthesis and Characterization of Triblock Copolymers Containing Amphiphilic Dendron

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Dendrimers/dendrons are regularly branched macromolecules which have received a great amount of attention due to their structural and physical uniqueness.¹ Recently, introduction of microphase-separation concept has been proved to lead to a self-assembling system which shares the morphological behavior of dendrimers/dendrons and linear block copolymers.²

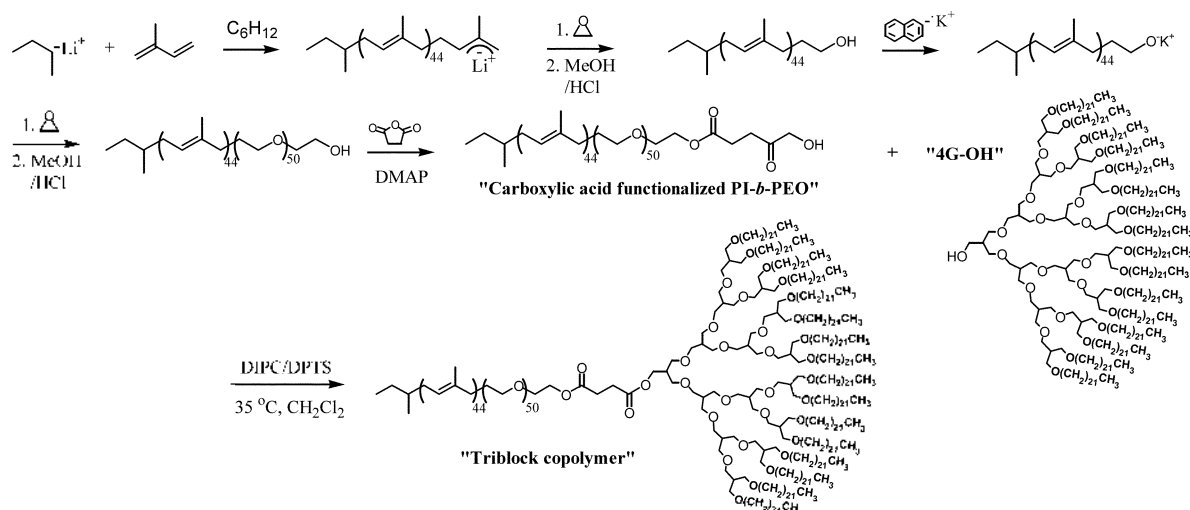
However, dendron and linear polymer fused system has not been extended to complicated chain architectures. For example, triblock copolymers, they have potential to self-organize into complex and exciting nanostructures such as a ring and a knitting pattern which can not be expected in conventional diblock copolymer systems.³ Therefore, it would be an interesting challenge to study the influence of dendron architecture on self-assembled nanostructures in triblock copolymer systems. To this end, we 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)].

As shown in Scheme 1, the synthesis began with anionic polymerization of isoprene.⁴ 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 oxyanion

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-O⁻K⁺. 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. 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 gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR) spectroscopy determines that the molecular weights of PEO and PI are 2170 and 3000 g/mol, respectively.⁵

Meanwhile, synthesis of an amphiphilic dendron (denoted as 4G-OH) was performed using a convergent synthetic method. The synthetic procedure consists of two organic reactions such as a Williamson etherification and hydroboration/oxidation reactions.⁶ Several iteration of these steps led to the monodisperse dendron, the synthetic details of which were reported previously.⁷

The triblock block copolymer was achieved through a simple esterification coupling reaction using *N,N'*-diisopropylcarbodiimide (DIPC) and 4-(dimethylamino)pyridinium-*p*-toluene sulfonate (DPTS). In this reaction, a two fold excess of 4G-OH with respect to PI-*b*-PEO was used to



Scheme 1. Synthesis of triblock copolymer.

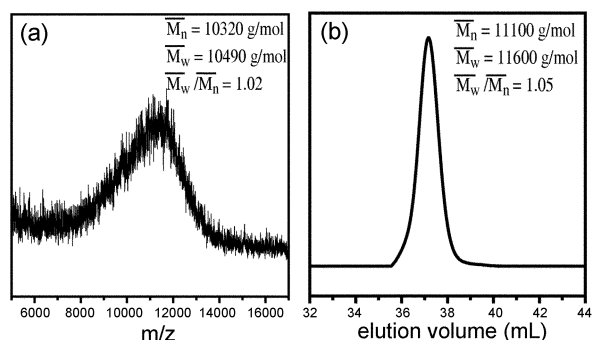


Figure 1. (a) Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrum and (b) GPC elugram of the triblock copolymer.

obtain high yield and purification convenience.

After the esterification reaction, the leftover 4G-OH was removed by column chromatography (silica gel) from chloroform-ethyl acetate (3 : 1 volume ratio) eluent, and then the triblock copolymer was collected by sequential column chromatography from chloroform-methanol (8 : 1 volume ratio) eluent. The molecular weight and polydispersity were characterized by mass spectrometry and GPC. The number average molecular weights (\bar{M}_n) from both techniques were estimated to be about 11,000 g/mol (10320 and 11100 g/mol from mass spectrometry and GPC, respectively), which are nearly consistent with the summation (11446 g/mol) of each molecular weight of PI-*b*-PEO and 4G-OH (Figure 1).

Three blocks are expected to show different thermal properties in the solid state due to their distinct segmental structures, which were characterized by differential scanning calorimetry (DSC). On both heating and cooling scans, two peaks were observed, corresponding to the melting transitions of PEO and docosyl peripheries, respectively. Compared to the docosyl chain melting temperature of 4G-OH (61 °C),⁷ the docosyl melting temperature of the triblock copolymer (59 °C) is almost comparable. This might be due to the fact that the other hydrophobic amorphous PI chains are not mixed with docosyl peripheries in the solid state. In addition, X-ray diffraction pattern at 20 °C shows two reflections with *q*-spacing ratio of 1 : 2, which are indicative of a lamellar structure consisting of periodic microphase-separated layers. Consequently, it can be suggested that all three blocks are microphase-separated in the solid state.

More remarkably, the PEO melting transition temperature in the triblock copolymer is significantly suppressed in comparison with that (52 °C) of homo-PEO (M.W. of 2,000 g/mol) or the carboxylic acid functionalized PI-*b*-PEO (44 °C). This might be originated from both the connectivity with the dendritic core and the similar chemical composition between the dendritic core and PEO. Since the cross sectional area of the dendron is much larger than that of PEO, PEOs have to be considerably folded in their crystalline layers in contrast to the cases of homo-PEO or PI-*b*-PEO, resulting in imperfection of PEO crystals.⁸ In addition, the dendritic core with amorphous liquid character is expected to be compatible with PEO chain with the nearly identical

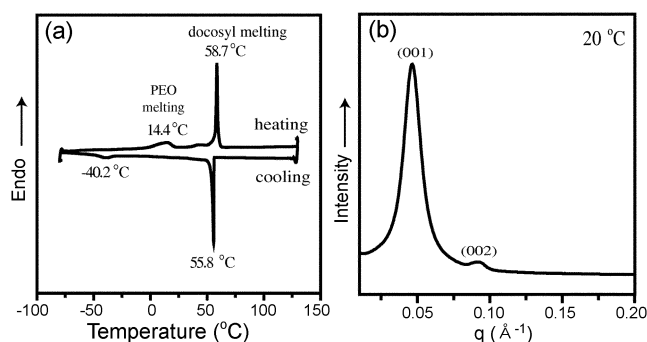


Figure 2. (a) DSC curves of second heating scan on the upper and first cooling scan on the lower of the triblock copolymer; (b) Small angle X-ray pattern of the triblock copolymer at 20 °C. The first and second transition peaks in each thermogram correspond to the PEO and docosyl group melting transitions, respectively.

chemical composition, similar to what was found in other systems.^{8,9}

In summary, 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 triblock copolymer. DSC and X-ray scattering results suggest that the three blocks are microphase-separated in the solid state.

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