Synthesis and Properties of Dendritic Polyamide-\(b\)-Poly(4-Vinylpyridine) Block Copolymers bearing Hydrogen Bonding Parts

Takayuki Kouketsu, Mitsutoshi Jikei, Teruaki Hayakawa, and Masa-aki Kakimoto

Department of Organic and Polymeric Materials, Tokyo Institute of Technology,
2-12-1, O-okayama, Meguro-ku, Tokyo 152-8550, Japan

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1. Introduction

Dendritic molecules present a number of new possibilities in the areas of molecular engineering and nanotechnology due to their unique structure and properties. This accurate control over the number and placement of functional groups permits the synthesis of a novel family of block copolymer, hybrid dendritic-linear systems in which a dendrimer is covalently attached to a linear polymer to give a diblock copolymer structure.

Gitsov, Wooley, and Fréchet reported the first to introduce dendritic-linear diblock copolymers by attaching convergently synthesized benzyl ether dendrons to one or both terminal end groups of linear poly(ethylene glycol) [1]. These diblock copolymers illustrated a range of interesting solvent dependent solution behavior. Meijer and co-workers also reported on the synthesis and properties of amphiphilic diblock copolymers of polystyrene and acid-functionalized polypropyleneimine dendrimer that exhibited generation-dependent aggregation in solution and microphase segregation in the solid state [2]. Although similar researches have recently been made by Hammond and co-workers [3] and Mackay et al. [4] with poly(benzyl ether)dendron or polyamideamine dendrons diblock copolymers, self-assembly of dendritic-linear diblock copolymers almost have been formed by an amphipilic property.

Hydrogen bonding is one of the important non-covalent interactions in nature because of its stability, dynamics, and directionality. If the varieties of hydrogen bonding moieties are strategically introduced into new polymeric materials having dynamic functions can be obtained.

In this work, we report the preparation and properties of new hybrid dendritic polyamide-\(b\)-poly(4-vinylpyridine) block copolymers bearing carboxylic acid and pyridine as hydrogen bond donor and acceptor, respectively.

2. Results and Discussion

A novel dendritic macriniitiator (Cl-G1-4COOH) bearing one benzyl chloride at the core and four carboxyl groups at the ends was synthesized by the six steps reaction, as shown in Scheme 1.

Scheme 1. Synthesis of dendritic macriniitiator bearing one benzyl chloride at the focal points and four carboxyl groups at the ends.
Table 1. ATRP of 4-Vinylpyridine Initiated by 7/CuCl/Me₅TREN.

<table>
<thead>
<tr>
<th>No.</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Solvent</th>
<th>Conc. (mol/L)</th>
<th>[M]/[I]/[Me₅TREN]</th>
<th>Conv. (%) b</th>
<th>Mₘ (Calc.) b</th>
<th>Mₘ (1H NMR)</th>
<th>DP</th>
</tr>
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<tr>
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<td>50</td>
<td>24</td>
<td>DMF</td>
<td>5</td>
<td>100/1/10</td>
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<td>2200</td>
<td>3000</td>
<td>20</td>
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<td>48</td>
<td>DMF</td>
<td>15</td>
<td>500/1/25</td>
<td>7</td>
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<td>8</td>
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<td>5600</td>
<td>45</td>
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<tr>
<td>4</td>
<td>50</td>
<td>24</td>
<td>DMSO</td>
<td>15</td>
<td>500/1/25</td>
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<tr>
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<td>4000</td>
<td>3300</td>
<td>23</td>
</tr>
</tbody>
</table>

a: Conversion determined by gravimetry.
b: Mₘ (Calc.) = ((([4-VP])/7] x MW₄vinylpyridine) x conversion) + MW₇.

Structure of 2, 3, 4, and 5 was confirmed by IR and 1H NMR spectroscopy. 6 was prepared by precipitation in aq HCl after the reaction 5 and glutaric anhydride. 7 was prepared by transform benzyl alcohol of 6 into benzyl chloride with triphenyl phosphine and CC1₄. In 1H NMR spectra, the chemical shift corresponding to the core of 7 was observed at 4.74 ppm, whereas hydroxyl signal at 4.48 ppm disappeared. In addition, infrared (IR), 13C NMR, and MALDI-TOF mass spectroscopy showed that the desired 7 was obtained in quantitative yield without a side product.

Dendritic polyamide-b-poly(4-vinylpyridine) block copolymers were synthesized by atom transfer radical polymerization of 4-vinylpyridine with 7 as an initiator, as shown in Scheme 2 [5].

Scheme 2. ATRP of 4-vinylpyridine with 7 as an initiator.

The ATRP of 4-vinylpyridine was carried out in DMF in the presence at 7, CuCl(I), tris[2-(dimethylamino)ethyl]amine (Me₅TREN) at 40 °C. After the polymerization, the solution was poured into diethyl ether, and then the precipitation was isolated. The results of polymerization of 4-vinylpyridine initiated by carboxylic-terminated dendron featuring benzyl chloride focal points are listed in Table 1. Under various conditions, a conversion of monomer was about 15%, presumably due to the significant coordination of the monomer or polymer to the catalyst and the formation of salts with carboxylic acid of initiator and Me₅TREN. When the polymerization of 4-vinylpyridine was carried out in methanol for 24 h, the polymerization was proceeded in homogeneously, and the conversion of monomer was 17%. The 1H NMR spectra showed that the desired dendritic-linear block copolymers were obtained. The number average molecular weight (Mₘ) of dendritic-linear block copolymer was estimated by NH signal of amide and pyridine signal analysis in 1H NMR spectrum. Mₘ was obtained by the ratio of integrated intensity for NH protons of amide to the pyridine protons at linear P4VP. Dendritic-linear block copolymer (Mₘ=4700) was closed to the calculated value (Mₘ=4500).

In summary, we have successfully prepared new hybrid dendritic-linear diblock copolymers bearing hydrogen bonding parts via ATRP of 4-vinylpyridine using 7 as an initiator. The resulting block copolymers might be assembled by the formation hydrogen bonding between carboxylic acid and pyridine.

References