Thermal Property of Phenylazomethine Dendrimer with Porphyrin Core

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Keywords: dendrimer, phenylazomethine, porphyrin,
weight decreasing temperature, glass transition

1. Introduction
Metallo-porphyrin complexes are well known to provide some key reactions in biological systems. [1] Because of their availability and interest, many researchers have focused on their application, e.g., as a reaction center of the molecular conversion and a sensitizer of the photo-energy conversion system. In particular, porphyrin-containing dendrimers, which can construct an ordered nano-space, were studied to mimic enzymatic reactions. [2] We have synthesized a new type of dendrimer, which has phenylazomethine substituents around the porphyrin core. [3] They are capable of assembling metal ions like the dendritic phenylazomethines (DPA) that we have already reported. [4] Because of the resemblance to enzymes bearing metal complexes around the reaction center, [5] it is expected to be a functional catalyst for synergy of the porphyrin core and metal-assembling dendrons.

To modify these molecules on surfaces for the purpose of preparing a functional monolayer or film the phenylazomethine dendrimer is also suitable for the easy preparation only by casting without any aggregation and transformation of the core units. [6] This advantage arises from the stiff structure, which is related to the π-conjugated backbones. In this regard, the thermal properties (melting and glass transition) should be important factors, but there have been few reports investigating the properties of rigid dendrimers, which have aroused our interests. This is the first report on the thermostabilities of phenylazomethine dendrimer by thermo-gravimetry (TG) and differential scanning calorimetry (DSC).

Figure 1. Structure of phenylazomethine dendron / dendrimers.

2. Method
The DPAs having a p-phenylene core and a porphyrin core were prepared as previously reported method. [3,6a]
TG measurements were carried out using a Rigaku TG8120. Samples were heated with alumina as a referential sample under N$_2$ flow, from 25 °C to 1000 °C with a rate at 20 °C/min. DSC experiments were measured using a Rigaku DSC8230 with the same instrument as the TG measurements from 25 °C to 300 °C. The heating was undergone with a rate at 40 °C/min, after the cooling with a rate at 10 °C/min.

![Graph](image)

**Figure 2.** 10 weight % decreasing temperatures of phenylazomethine dendrimers with porphyrin core (solid: G1, dash dot dash: G2, dash dot dash: G3, short dash: G4).

<table>
<thead>
<tr>
<th>Generation number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{d-10%}$ (°C)</td>
<td>531</td>
<td>528</td>
<td>523</td>
<td>531</td>
</tr>
</tbody>
</table>

**Table 1.** 10% weight decreasing temperatures of porphyrin dendrimers.

3. Results and discussion

We have previously reported that the polyphenylazomethine structure has resisting property associated with heat decomposition. Thus, the weight losses of the porphyrin core dendrimers during the heating process were studied. Each generation number of DPAs with a porphyrin cores showed 10 weight % decreasing temperatures ($T_{d-10\%}$) over 520 °C (Table 1). This means that the sequence of DPAs with the porphyrin core has a high heat-resisting property and has an extremely tough structure resulting from all $\pi$-conjugated backbones. The $T_{d-10\%}$ values were higher than the DPAs with the phenylene core, suggesting that the doubled increase on the number of phenylazomethine substituents resulted in a greater conformational restriction and petrifaction. In addition, polyphenylazomethine, the linear-type complement of our dendrimer, is equivalent or lower in thermostability.

Depending upon the physical properties, there are observed three types of phase transition on the DSC curve, i.e., melting, crystallization and glass transition. When heating a sample, an endothermic peak indicates the melting point of a highly crystallized solid or the glass transition point of an amorphous-favor substance. The glass transition peaks for the polymers generally tend to broaden and to become stair-shaped curves, because of the range of segment lengths. [7]

First of all, we examined the phenylazomethane dendron, which is a prototypical substituent of DPAs without cores, in order to know the fundamental characteristics. Especially, the dendron G3 was used because it could easily change its phase between crystalline and amorphous. The crystalized dendron showed a small endothermic peak at 145 °C on the second heating curve, whereas a large endothermic peak was observed at 269 °C on the first heating (Figure 3). This indicates that the glass transition of dendron G3 was caused by the cooling. In the case of dendron G3 not crystallized after its syntheses, $T_g$ was around 135 °C. DSC curves depend on the thermal histories of dendrimers of the materials. These temperature changes are very similar with the aging of polymers, [7-8] and accordingly, the difference in the $T_g$ for non-crystalized dendrons is considered to be a result of the crystallinestates in the amorphous dendrons still partially remaining even through
heating process.

Next we investigated the p-phenylene core dendrimers of each generation number. They had higher $T_g$s than dendron G3 except the G1 (Table 2), because it was such a small molecular that we could not consider it to be a kind of polymers. Their transition points increase with the generation numbers.

![Graph showing heat flow vs. temperature (1st and 2nd cycle)](image)

Figure 3. Heating standard DSC experiments with $q_a = +40 ^\circ\text{C}/\text{min}$ (2nd cycle: after a cooling with $q_a = -10 ^\circ\text{C}/\text{min}$).

<table>
<thead>
<tr>
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<th>4</th>
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<tbody>
<tr>
<td>dendron</td>
<td>135 (145)$^a$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-phenylene dendrimer</td>
<td>50</td>
<td>148</td>
<td>174</td>
<td>188</td>
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<tr>
<td>porphyrin dendrimer</td>
<td>195</td>
<td>201</td>
<td></td>
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</tr>
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</table>

Table 2. Glass transition temperatures ($^\circ\text{C}$) of phenylazomethine dendron and dendrimers.

a) The value in parenthesis is the temperature of crystallized sample obtained during 2nd heating.

The last measurements were of the porphyrin core dendrimers, and characteristic glass transition temperatures were observed above dendrimer G3. Dendrimers G1 and G2 did not show any obvious transitions because the porphyrin core, occupying a large part of the molecule, prevents simultaneous micro-Brownian motion. In contrast, with dendrimers having advanced sequences of substituents, a simultaneous phase transition took place due to the strong characteristic of the poly-phenylazomethine backbones. Comparing between dendron G3 and dendrimers G3 with the porphyrin core or pphenylene core, an improvement in the $T_g$ was seen from 135 $^\circ\text{C}$ to 174 $^\circ\text{C}$ or 195 $^\circ\text{C}$ as the substituent numbers.

Overall, the transition temperatures increased with the generation numbers and substituent numbers. This was caused by the spatial restriction with results similar to the TG measurements. We can now say that the thermal performance of the porphyrin dendrimer is also comparable enough to other polymers-like versatile engineering plastics [9].

**Acknowledgement**

This work is partially supported by a Grant-in-Aid for Priority Area, for scientific research, and 21st century COE program (Keio-TCC) from the Ministry of Education, Culture, Sports, Science & Technology Foundation, a Grant-in-Aid for evaluative technology (CREST) from the Science and Technology Agency, and Kanagawa Academy science and technology research grant (project No. 23).

**References**