

# An Aromatic Polyether Ketone Supported Organocatalyst for Selective Aerobic Oxidation of Alcohols

○Ying Shi, Yuta Nabae, Teruaki Hayakawa, Masa-aki Kakimoto \*

Department of Organic and Polymeric Materials, Graduate School of Science and Engineering,  
Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

E-mail: [mkakimot@o.cc.titech.ac.jp](mailto:mkakimot@o.cc.titech.ac.jp)

**Abstract:** A hyperbranched aromatic polyetherketone with carboxylic acid terminal groups was synthesized to immobilize catalytically active species such as 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO). The synthesized catalyst shows a good catalytic activity and selectivity for the aerobic oxidation of alcohols in a nitric acid-assisted carbon-catalyzed oxidation system. The catalyst combines the benefits of both homogeneous and heterogeneous.

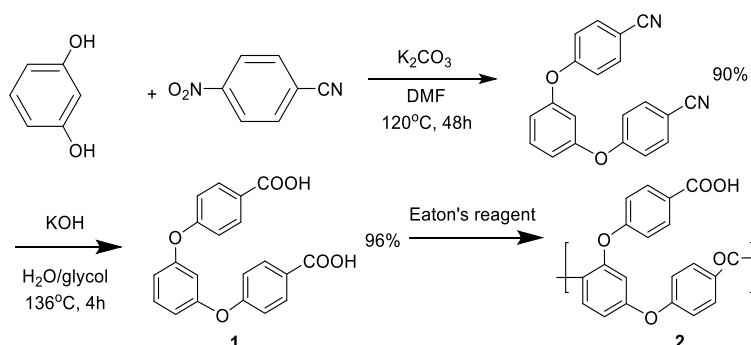
## 1. Introduction

Selective oxidation of alcohols to aldehydes is of great importance.

2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), as an efficient non-metallic catalyst, has been immobilized to various supports for efficient recycling. Hyperbranched polyether ketone has high thermal stability and a large number of functional terminal groups which can immobilize TEMPO with a high loading rate.

## 2. Experimental

The hyperbranched aromatic polyetherketone was synthesized as shown in Scheme 1. Resorcinol and 4-nitrobenzonitrile were reacted under an aromatic nucleophilic replacement condition in the presence of potassium carbonate to form 4,4'-(m-phenylenedioxy)-bisbenzenenitrile. And then a basic hydrolysis reaction successfully converted the nitrile terminals to carboxylic acid terminals to obtain the AB<sub>2</sub> type monomer (**1**), 4,4'-(m-phenylenedioxy)-bis(benzenecarboxyl acid). The structure of **1** was characterized by proton NMR (Figure 1a) and IR spectroscopy (1670, C=O stretching; 2500-3000, O-H vibration, broadband).



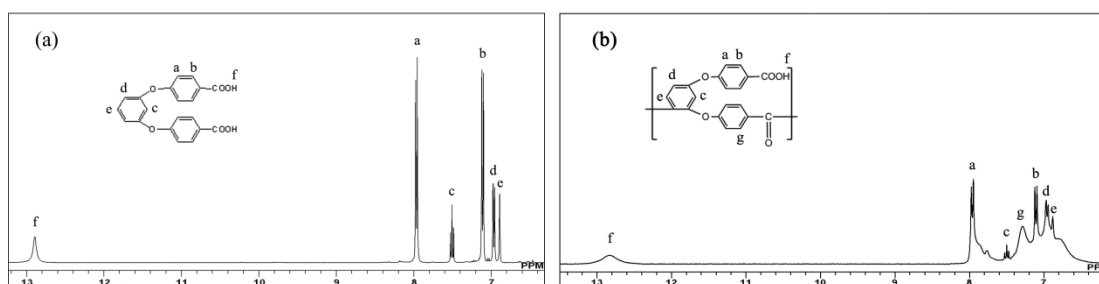
**Scheme 1** Synthesis and structures of hyperbranched polyetherketone possessing carboxylic acid as terminal groups.

The molecular weights were determined by gel permeation chromatography (GPC) using a

Viscotek TDA 302 system with a TSK-GEL  $\alpha$ -M column and *N,N*-dimethylformamide (DMF) as eluent. Catalyst reaction was analyzed with a SHIMAZDU GCMS-QP2010 Plus, using a GL Sciences TC-FFAP column.

### 3. Results and discussion

Self-polycondensation of **1** was carried out in PPMA solution (Eaton's reagent, 7.7 wt% phosphorus pentoxide solution in methanesulfonic acid) <sup>1</sup>. After polymerization, the peak of carboxyl acid (f, 12.89 ppm) decreased and a new peak g (7.28 ppm) appeared (Figure 1) in <sup>1</sup>H NMR spectra, which supported successful polycondensation.



**Figure 1** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) of monomer **1** (a) and polymer **2** (b). The decreased carboxyl acid peak at 12.89 ppm and the new peak at 7.28 ppm demonstrated the process of polycondensation.

The polycondensation proceeded smoothly under 110°C, giving hyperbranched polymer with different weight-average molecular weights which was determined by GPC after changing the terminal to ethyl ester group. The molecular weight of polymer can be controlled by changing polymerization conditions. Some results are summarized in Table 1.

The ion exchange capacity (IEC) in each polymer was calculated by titration. Entry a shows an IEC of 2.8 mol kg<sup>-1</sup>, while the theoretical value is 2.9 mol kg<sup>-1</sup>. As the weight-average molecular weight increasing, the amount of hydrogen decreased. It is supposed that cross-linking which leads to an obviously large weight-average molecular weight consumed some carboxylic acid terminal groups.

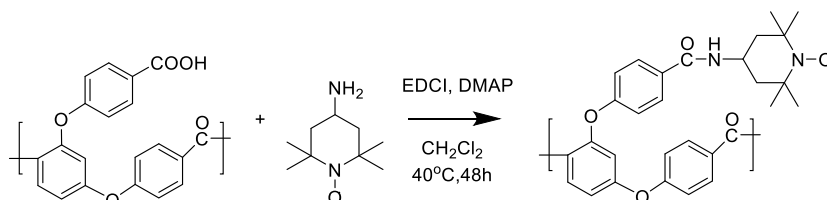
**Table 1.** Synthesis of hyperbranched polymer **2** under different conditions

Entry	PPMA /mL	T/°C	Time /h	<i>M</i> <sub>w</sub> <sup>a</sup>	Yield	IEC /mol kg <sup>-1</sup>
a	3	110	2	42000	84	2.8
b	2	110	2	74000	84	2.5
c	2	110	6	123000	94	2.3
d	2	110	10	159000	92	2.2

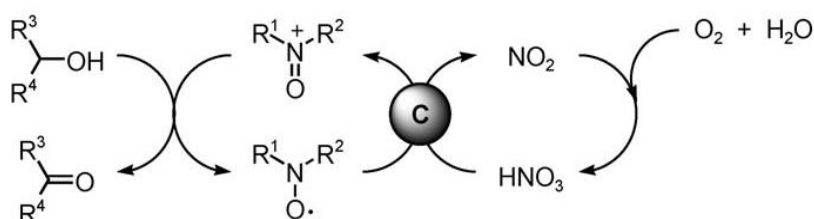
<sup>a</sup>Determined by GPC eluted with DMF containing lithium bromide (0.05 mol/L).

Entry a, with highest IEC was chosen to loading TEMPO in following experiments. The hyperbranched polymer was linked with TEMPO via Scheme 2. After fully washing the sample

with acetone and drying, elemental analysis was carried out. According to the Nitrogen content, the TEMPO loading was determined as 1.9 mmol g<sup>-1</sup>, suggesting that over 88% terminal was linked with TEMPO.



Scheme 2. Hyperbranched polymer linked with TEMPO



Scheme 3. Nitroxide radical-NACOS

Thus obtained TEMPO loaded polymer was tested as a catalyst for the selective aerobic oxidation of alcohols in nitric acid-assisted carbon-catalyzed oxidation system (NACOS) (Scheme 3).<sup>2</sup> In the benzyl alcohol oxidation with 0.8% mole ratio of TEMPO units on polymer and 8% mole ratio of HNO<sub>3</sub>, the conversion reached 91.6% under 90 °C after 3h, and the selectivity to benzaldehyde was over 99% (Table 1, entry 3). The catalyst can be easily recycled with the help of Ketjen black by simple filtration, and the collection yield can reach over 99%.

**Table 2.** Aerobic oxidation of benzyl alcohols.

Entry	Benzyl alcohol	TEMPO units on polymer	Ketjen black	HNO <sub>3</sub>	Conv.% <sup>a</sup>	Sel.%
1	10mmol	0.8mol%	0	8mol%	45.8	>99
2	10mmol	0	50mg	8mol%	6.4	93
3	10mmol	0.8mol%	50mg	8mol%	91.6	>99
4	10mmol	Commercial TEMPO 0.8mol%	50mg	8mol%	94.9	>99

[a] Reaction condition: Polymer catalyst 42mg, Commercial TEMPO 12.5mg, Nitric acid 27 μ L, 90°C, 3h, Oxygen atmosphere

#### 4. Conclusions

A hyperbranched aromatic polyetherketone has been synthesized to immobilize TEMPO as a new catalyst. The synthesized catalyst shows a good catalytic activity and selectivity for the aerobic oxidation of primary alcohols. Recycling test requires to be done in more detail

studies to prove the recyclability of the designed catalyst.

### References

1. J. Hao, M. Jikei, M. Kakimoto, *Macromolecules*, 35, 5372 (2002)
2. Y. Kuang, H. Rokubuichi, Y. Nabaе, T. Hayakawa, M. Kakimotoa, *Adv. Synth. Catal*, 352, 2635 (2010)