Electrooxidation of Alcohols in an *N*-Oxyl Immobilized Rigid Polymer Particles Disperse Water System.

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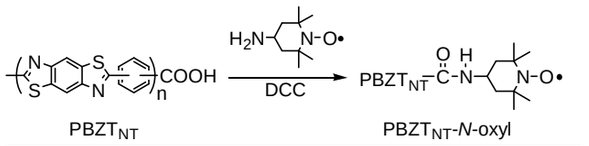
Electrooxidation of alcohols mediated with *N*-oxyl compounds has been intensively investigated as a prominent tool for organic synthesis. So far reported *N*-oxyl mediated electrooxidation are mainly performed in polar organic solvents containing high concentration of supporting electrolytes to afford good to excellent yields of the corresponding ketones and/or aldehydes, but not necessarily satisfactory in terms of operational simplicity, manufacturing cost, and environmental stress arising from use of polar organic solvents. To overcome these problems, we developed electrooxidation in *N*-oxyl-immobilized solid particles disperse-water systems, wherein water-insoluble alcohols were supported on the *N*-oxyl-immobilized disperse phase such as silica gel and polymer particles.[1,2] Recycle use of the mediator could be performed successfully,[3] thereby offering a completely closed oxidation system. The disperse phase, *e. g*., silica gel and polymer (polyethylene and poly(ethylene-*co*- acrylic acid) particles, however, suffered significant degradation during the course of the recycle use. Therefore, mechanically tough solid particle is more desirable in practical sense. In our continuing studies, we investigated use of poly(*p*-phenylene benzobisthiazole) network polymer ($PBZT_{NT}$, rigid-rod polymer) for the disperse phase. Herein we describe that the $PBZT_{NT}$ particles were strong enough to survive without significant change of their shape and size even after 60 times recycle use, and *N*-oxyl-immobilized $PBZT_{NT}$ efficiently promoted electrooxidation of alcohols.

N-oxyl-immobilized $PBZT_{NT}$ was prepared as follows (**Scheme 1)**. $PBZT_{NT}$ (400 mg) was treated with 4-amino-TEMPO (0.6 mmol) in acetonitrile in the presence of DCC (0.7 mmol) at 50 ºC for 2 days. The polymer particles were filtrated, washed with acetonitrile, and dried under vacuum to give the *N*-oxyl-immobilized $PBZT_{NT}$.

A typical procedure of the electrooxidation of alcohols in an *N*-oxyl-immobilized $PBZT_{NT}$ disperse water system is as follows (**Fig. 1**). A mixture of *N*-oxyl-immobilized $PBZT_{NT}$ (450 mg), alcohol **1a** (0.5 mmol) in an aqueous sodium hydrogencarbonate containing 20 wt% sodium bromide was placed in a simple undivided cell. Two platinum electrodes were immersed into the reaction mixture, and a constant current (20 mA, 2.5 F/mol) was supplied under vigorous stirring to afford the corresponding ketone **2a** in good yield (**Fig. 2, Run 1**). The recovered *N*-oxyl-immobilized $PBZT_{NT}$ could be repeatedly used for the subsequent electrooxidation of **1a** without significant change of the yield of **2a** (**Runs 2~5**). The yield of ketone gradually decreased after 20 runs and reached to 50% after 30 runs. The yield of **2a** was restored by treatment of the recovered *N*-oxyl-immobilized $PBZT_{NT}$ with 4-amino-TEMPO (**Runs 32, 58**). The appreciable change of shape of the polymer was not detected. The representative results of electrooxidation of several alcohols **1** in this system are shown in **Table 1**.

Scheme 1. Preparation of *N*-Oxyl-Immobilized $PBZT_{NT}$



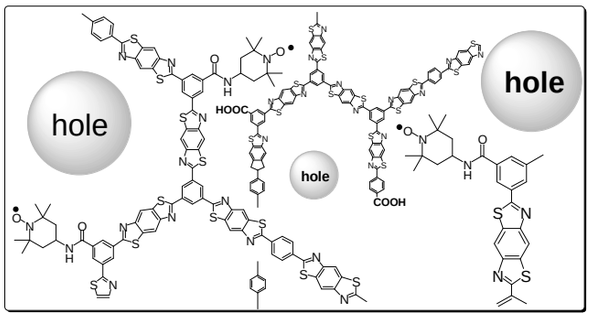


Fig. 1. Totally Closed System

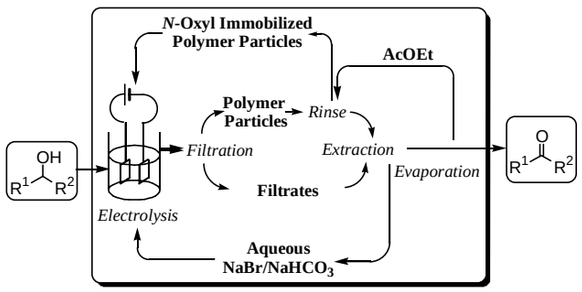
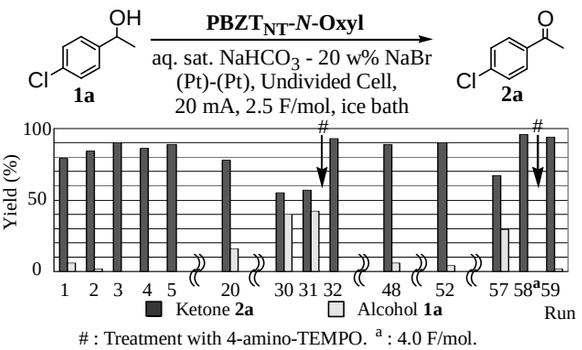
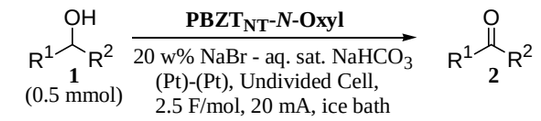


Fig. 2. Recycle Use of *N*-Oxyl-Immobilized $PBZT_{NT}$



: Treatment with 4-amino-TEMPO. [a] : 4.0 F/mol.

Table 1. Electrooxidation of Alcohols in *N*-Oxyl-Immobilized $PBZT_{NT}$-Disperse Water System



Alcohol	**1b**	**1c**	**1d**	**1e**
Product	**2b**	**2c**	**2d**	**2e**
Yield	**84%**	**73%**	**37% (79%)[a]**	**90%[b]**

[a] CH_3CN (1.5 ml) was used as co-solvent. [b] 4.0 F/mol

References:

1) H. Tanaka, et al. The 197th Meeting of ECS, Abstr. No. 1087. *Tetrahedron Lett*. **2001**, *42*(3), 445-448.

2) H. Tanaka, et al. The 199th Meeting of ECS, Abstr. No.959.

3) H. Tanaka, et al. 2001 Joint International Meeting, Abstr. No. 1207.