



PolyTEMPO electrocatalyst for organic electrosynthesis of benzonitrile from benzyl alcohol

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ABSTRACT

Requirements for using Poly (2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PolyTEMPO) as an electrocatalyst for the organic electrosynthesis of benzonitrile from benzyl alcohol were investigated. The research results indicated that PolyTEMPO expressed catalytic activity in the electrosynthesis of benzonitrile from benzyl alcohol in the presence of ammonium acetate. The electrosynthesis yield of benzonitrile from benzyl alcohol with PolyTEMPO catalyst reached the maximum value at 35 °C after 18 hours.

Introduction

Benzonitrile is an important organic compound due to its use as an intermediate for rubber chemicals and as a solvent for nitrile rubbers, resins, polymers, specialized lacquers and anhydrous metallic salts. There are many methods of synthesizing benzonitrile. However, classical methods using redox agents show several disadvantages, such as low selectivity, high temperature and use of toxic metal cyanides [1]. Meanwhile, electrosynthesis processes offer several economic, ecologic and practical advantages compared to classical methods [1]. The use of electric current instead of redox reagents provides the opportunity for reducing cost, waste generation and energy consumption. Therefore, for the synthesis of benzonitrile, electrosynthesis methods using external current have been considered new directions.

In organic electrosynthesis processes, electrocatalysts play important roles. Among them, 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) has been selected

as a robust, versatile and well-characterized catalyst for many organic electrosynthesis processes, including oxidation of alcohols, sulfides, thioamides and organometallic compounds [2, 3, 4]. Besides, the attachment of electrocatalysts to soluble polymer backbones to create a homogeneous electrolyte represents a promising approach for improving both ionic conductivity and electron transfer kinetics [5]. In our group's previous work, fabricated PolyTEMPO was used as a soluble electrocatalyst for the electrooxidation of alcohols to carbonyl compounds [5]. In this work, we have continued to investigate requirements for using fabricated PolyTEMPO as an electrocatalyst for the electrosynthesis of benzonitrile from benzyl alcohol in the presence of ammonium acetate.

Experimental

Chemicals

$C_6H_5CH_2OH$ (benzyl alcohol), CH_3CN (acetonitrile), $LiClO_4$ (lithium perchlorate), $AgNO_3$ (silver nitrate), NBu_4ClO_4 (tetrabutylammonium perchlorate), CH_3COONH_4 (ammonium acetate), $C_9H_{12}O_3$ (2,4,6-trimethoxybenzene), and benzonitrile (C_6H_5CN) were purchased from Tokyo Chemical Industry Company. All the chemicals were of analytical grade.

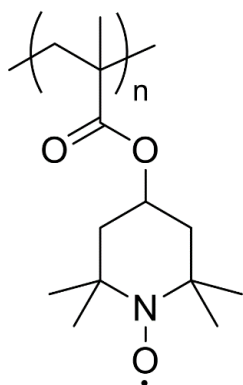


Figure 1: Structure of PolyTEMPO

Poly (2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PolyTEMPO) was synthesized using the synthesis procedure described in our previous work [5]. The structure of PolyTEMPO is shown in Figure 1.

Cyclic voltammetry study

Cyclic voltammetry (CV) technique was used to investigate the electrocatalytic activity of PolyTEMPO for electro-synthesis of benzonitrile from benzyl alcohol. Cyclic voltammetric measurements were performed on a Parstat 4000 (Princeton Applied Research) using a three-electrode cell set-up with 0.1 M $LiClO_4-CH_3CN$ as electrolyte. The potential was swept between 0–1.5 V at a scan rate of 50 mV s^{-1} . The working electrodes were Pt or glassy carbon electrodes, which were polished with corresponding polishing cloths before measurement. The areas of the working electrodes were 0.0707 cm^2 . The counter electrode was a Pt wire. The reference electrode was a $Ag/AgNO_3$ electrode (silver wire in 0.1 M NBu_4ClO_4/CH_3CN solution; $C(AgNO_3) = 0.01\text{ M}$; $E_0 = -87\text{ mV}$ vs. ferrocene redox couple) [6]. The electrolyte was purged with argon for at least five minutes prior to recording the CVs.

Electrolysis

Chronoamperometry technique was used to investigate the efficiency of electro-synthesis of benzonitrile from benzyl alcohol using PolyTEMPO as the electrocatalyst. Potentiostatic electrolysis experiments were performed using the Parstat 4000 (Princeton Applied Research) with an undivided cell

containing 0.1 M $NBu_4ClO_4-CH_3CN$ solution (15 mL), benzyl alcohol (1.0 mmol), PolyTEMPO (0.15 mmol, 0.3 mmol or 1.0 mmol) and CH_3COONH_4 (3.0 mmol) at a constant potential of 1.5 V, 1.2 V, 1.1 V or 0.8 V with a magnetic stirring bar. The electro-synthesis conditions of benzonitrile from benzyl alcohol with PolyTEMPO catalyst can be shown in Figure 2. The electrolyte was purged with argon for at least five minutes prior to performing electrolysis. The undivided cell includes two electrodes, in which the cathode electrode is a Pt sheet (3.0 cm^2) and the anode electrode is a Pt sheet (3.0 cm^2) or a fabricated carbon roving bundle electrode (Torayca® T700 / 12k / 800 tex) [5]. The distance between the cathode and the anode was about 1.5 cm. Electrolysis processes for the synthesis of benzonitrile from benzyl alcohol using PolyTEMPO electrocatalyst were conducted at $35\text{ }^\circ\text{C}$ for 18 hours. In these electrolysis experiments, NBu_4ClO_4 was used instead of $LiClO_4$ as in the above CV experiments because the prolonged electrolysis time could lead to the formation of a Li film on the Pt cathode electrode.

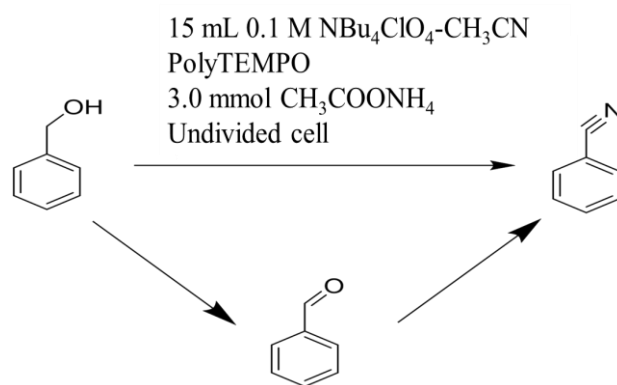


Figure 2: Electro-synthesis of benzonitrile from benzyl alcohol with PolyTEMPO catalyst

The mass of product of electrolysis (benzonitrile) were identified using gas chromatography (GC). GC measurements were carried out using a HP 1100 (Thermo Fisher) equipped with a 30 m HP5 column. Firstly, 128.5 mg of benzonitrile and acetonitrile were added to a volumetric flask to obtain 25 mL of solution. Vials which contain different volumes (20, 40, 80, 120, 160, and 200 μL) of the above benzonitrile solution, 50 μL of 2,4,6-trimethoxybenzene (as an internal standard), and 1 mL of acetonitrile, were prepared for GC measurements. A calibration curve of A_{BN}/A_{IS} vs. m_{BN} was built using GC results, in which A_{BN} and A_{IS} are areas of peaks corresponding to benzonitrile and 2,4,6-trimethoxybenzene, respectively, and m_{BN} (mg) is mass of benzonitrile in 25 mL of solution. Secondly, after electro-synthesis of benzonitrile from benzyl alcohol, all products were collected, and acetonitrile

was added to obtain 25 mL of solution. A vial which contains 200 μL of the product solution, 50 μL of 2,4,6-trimethoxybenzene, and 1 mL of acetonitrile was prepared for a GC measurement. Then the GC result and the calibration curve of $A_{\text{BN}}/A_{\text{IS}}$ vs. m_{BN} were used to determine the mass of obtained benzonitrile and to calculate the yield of electrolysis.

Results and discussion

Cyclic voltammetry results

The electrochemical oxidation process of benzyl alcohol to benzonitrile with PolyTEMPO catalyst and $\text{CH}_3\text{COONH}_4$ was investigated in $\text{LiClO}_4\text{-CH}_3\text{CN}$ solution. $\text{CH}_3\text{COONH}_4$ was used as the nitrogen source. Figure 3 shows cyclic voltammograms of the Pt working electrode measured in 10 mL of 0.1 M $\text{LiClO}_4\text{-CH}_3\text{CN}$ solution containing: 0.05 mmol PolyTEMPO (a); 0.05 mmol PolyTEMPO and 0.33 mmol benzyl alcohol (b); 0.05 mmol PolyTEMPO, 0.33 mmol benzyl alcohol, 1 mmol $\text{CH}_3\text{COONH}_4$ and 0.5 mL H_2O (c).

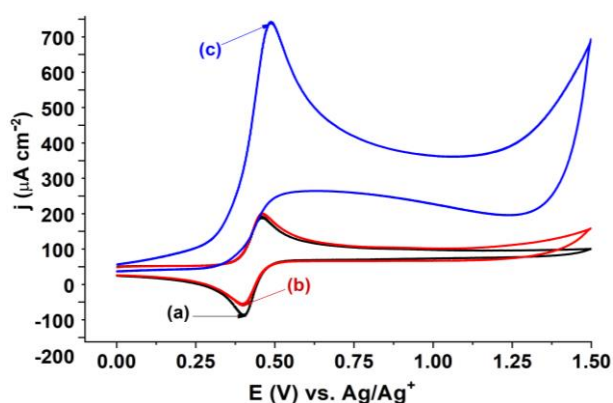


Figure 3: Cyclic voltammograms of the Pt working electrode measured in 10 mL of 0.1 M $\text{LiClO}_4\text{-CH}_3\text{CN}$ solution containing: 0.05 mmol PolyTEMPO (a); 0.05 mmol PolyTEMPO and 0.33 mmol benzyl alcohol (b); 0.05 mmol PolyTEMPO, 0.33 mmol benzyl alcohol, 1 mmol $\text{CH}_3\text{COONH}_4$ and 0.5 mL H_2O (c); (scan rate: 50 mV s^{-1})

Figure 4 shows cyclic voltammograms of the glassy carbon electrode measured in 10 mL of 0.1 M $\text{LiClO}_4\text{-CH}_3\text{CN}$ solution containing: 0.05 mmol PolyTEMPO (a); 0.05 mmol PolyTEMPO and 0.33 mmol benzyl alcohol (b); 0.05 mmol PolyTEMPO, 0.33 mmol benzyl alcohol, 1 mmol $\text{CH}_3\text{COONH}_4$ and 0.5 mL H_2O (c).

As can be seen in Figure 3a and Figure 4a, a pair of redox peaks at 0.458 V and 0.400 V represents to the one electron reversible generation of the catalytically-active oxoammonium ions (PolyTEMPO^+) from PolyTEMPO [1, 4]. As observed in Figure 3b and Figure

4b, when 0.33 mmol benzyl alcohol was added into the solution, there was no change in the cyclic voltammograms compared to the ones in Figure 3a and Figure 4a. These results indicated that there was no reaction between benzyl alcohol and PolyTEMPO^+ on the electrode surface.

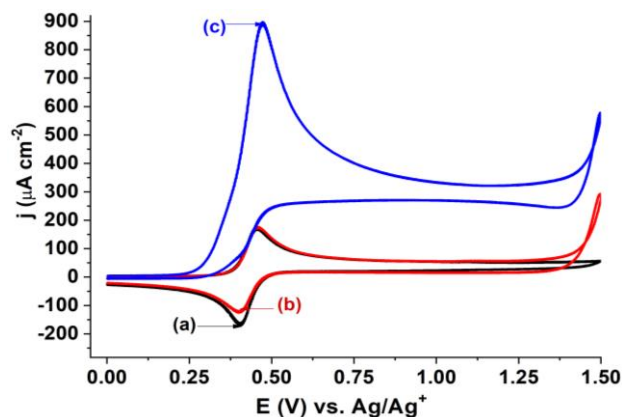


Figure 4: Cyclic voltammograms of the glassy carbon electrode measured in 10 mL of 0.1 M $\text{LiClO}_4\text{-CH}_3\text{CN}$ solution containing: 0.05 mmol PolyTEMPO (a); 0.05 mmol PolyTEMPO and 0.33 mmol benzyl alcohol (b); 0.05 mmol PolyTEMPO, 0.33 mmol benzyl alcohol, 1 mmol $\text{CH}_3\text{COONH}_4$ and 0.5 mL H_2O (c); (scan rate: 50 mV s^{-1})

As shown in Figure 3c and Figure 4c, when 0.33 mmol benzyl alcohol and 1 mmol $\text{CH}_3\text{COONH}_4$ were added into the solution, PolyTEMPO expressed catalytic activity in the electro-synthesis of benzonitrile from benzyl alcohol in the presence of $\text{CH}_3\text{COONH}_4$ as the nitrogen source [1]. The anodic peak current at 0.458 V increased significantly, which indicated that the generation of PolyTEMPO^+ from PolyTEMPO was stronger when adding $\text{CH}_3\text{COONH}_4$ into the electrolyte solution. This result also showed that the redox-catalytic process between benzyl alcohol and PolyTEMPO^+ was promoted by the addition of $\text{CH}_3\text{COONH}_4$. The cathodic peak disappeared, which showed that PolyTEMPO played the role as the electrocatalyst for oxidation of benzyl alcohol to benzonitrile in the presence of $\text{CH}_3\text{COONH}_4$.

Electrosynthesis of benzonitrile from benzyl alcohol with PolyTEMPO catalyst

The calibration curve of $A_{\text{BN}}/A_{\text{IS}}$ vs. m_{BN} is shown in Figure 5. There is a good linear relationship between $A_{\text{BN}}/A_{\text{IS}}$ and m_{BN} . The linear equation is $A_{\text{BN}}/A_{\text{IS}} = 0.02715m_{\text{BN}} - 0.2027$ with the correlation coefficient of $R^2 = 0.9980$. After electro-synthesis experiments, this calibration curve and GC results were used to calculate the mass of obtained benzonitrile and the yield of

electrolysis. The results of electrosynthesis of benzonitrile from benzyl alcohol with PolyTEMPO catalyst are shown in Table 1.

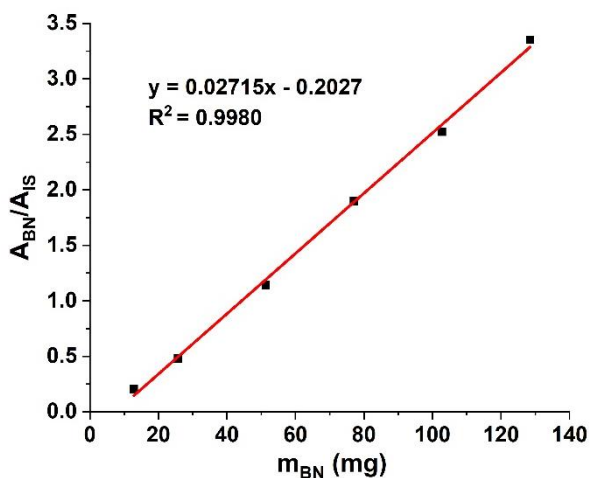


Figure 5: Calibration curve of A_{BN}/A_{IS} vs. m_{BN}

Table 1: Electrolysis for synthesis of benzonitrile from benzyl alcohol

Solvent	Catalyst	WE	Volt (V)	Yield (%)
CH ₃ CN	No	Bundle	1.5	2
CH ₃ CN	PolyTEMPO 15 %mol	Pt	1.5	1
CH ₃ CN	PolyTEMPO 100 %mol	Bundle	1.5	40
CH ₃ CN + 2,6-lutidine	PolyTEMPO 15 %mol	Bundle	1.5	15
CH ₃ CN	PolyTEMPO 30 %mol	Bundle	1.2	5
CH ₃ CN	PolyTEMPO 30 %mol	Bundle	1.1	7
CH ₃ CN	PolyTEMPO 30 %mol	Bundle	0.8	8

The electrosynthesis yield of benzonitrile from benzyl alcohol without electrocatalyst only reached 2 %. When the anode electrode was a Pt sheet, the yield of electrosynthesis of benzonitrile from benzyl alcohol with PolyTEMPO catalyst only reached 1 %. This result is explained that the Pt electrode was passivated by the presence of PolyTEMPO. Therefore, with using PolyTEMPO as a redox catalyst for electrosynthesis of benzonitrile from benzyl alcohol, the Pt electrode was replaced by the fabricated carbon roving bundle electrode.

When the anode electrode was the fabricated carbon roving bundle electrode, the yield of electrolysis for synthesis of benzonitrile from benzyl alcohol with PolyTEMPO catalyst reached the maximum value, 40 %, at the voltage of 1.5 V. When the voltage was 1.2 V, 1.1 V, and 0.8 V, the yield of electrolysis was only 5 %, 7 %, and 8 %, respectively. So the value of voltage

selected for the potentiostatic electrolysis was 1.5 V. When changing the solvent from acetonitrile (CH₃CN) to acetonitrile and 2,6-lutidine, the yield of electrolysis was only 15 %. Therefore, in this work, the condition for electrosynthesis of benzonitrile from benzyl alcohol was performing potentiostatic electrolysis (1.5 V) with PolyTEMPO catalyst, acetonitrile solvent and the fabricated carbon roving bundle electrode as the anode electrode.

Conclusion

In this study, the fabricated PolyTEMPO material was used as the electrocatalyst for electrosynthesis of benzonitrile from benzyl alcohol. The results indicated that PolyTEMPO expressed catalytic activity in the electrosynthesis of benzonitrile from benzyl alcohol in the presence of ammonium acetate as the nitrogen source. The electrosynthesis yield of benzonitrile from benzyl alcohol with PolyTEMPO catalyst reached the maximum value, 40 %, at 35 °C after 18 hours. The electrosynthesis experiments should be continued to find improved ways for performing electrolysis with higher yield.

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References

1. Z. Fan, X. Yang, C. Chen, Z. Shen, M. Li, J. Electrochem. Soc., 164(4) (2017) 54-58. <https://doi.org/10.1149/2.1561704jes>.
2. X. Y. Qian, S. Q. Li, J. Song, H. C. Xu, ACS Catal., 7(4)(2017) 2730-2734. <https://doi.org/10.1021/acscatal.7b00426>.
3. S. Li, L. Cheng, Q. Wu, Q. Zhang, J. Yang, J. Liu, ChemistrySelect, 3(4)(2018) 1268-1274. <https://doi.org/10.1002/slct.201702755>.
4. L. T. Tran, B. Schille, R. Francke, Vietnam J. Catal. Ads. 8(4)(2019) 128-131.

5. B. Schille, N. O. Giltzau, R. Francke, *Angewandte Chemie International Edition in English* 57(2)(2018) 422-426. <https://doi.org/10.1002/anie.201710659>.
6. T. Broese, R. Francke, *Org. Lett.*, 18(22)(2016) 5896-5899. <https://doi.org/10.1021/acs.orglett.6b02979>.