Supporting Information

Immobilization of Hydroquinone through a Spacer to Polymer Grafted on Carbon Black for a High-Surface-Area Biofuel Cell Electrode

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Experimental Methods

Detailed Experimental Procedures for Immobilization of Hydroquinone with Linear Polymers

Synthesis of pAc, phHAc and pcHAc

The polymerization reaction was conducted in dimethylformamide (DMF) using 0.01 mol/L azobisisobutyronitrile (AIBN) as initiator. The total monomer concentration in solution was fixed at 1 mol/L. For pcHAc, the molar ratio of AmHAc to AAm in the monomer solution was 1:1. After deaeration of the reaction mixture under vacuum and bubbling nitrogen gas through it, polymerization took place over 24 h at 70 °C. After the reaction was complete, the pAc reaction solution was poured into chloroform, and the phHAc and pcHAc solutions into acetone, to precipitate the polymers. After filtration, the polymer obtained was further purified by reprecipitation from DMF (for pAc and pcHAc) or ethanol (phHAc), with an excess amount of the solvent being used in the first precipitation. The resulting polymer was dried in vacuo at 50 °C for 24 h. The same drying condition was used throughout all experiments unless otherwise stated.

Direct Immobilization of Hydroquinone to pAc (pAcQ, Scheme 1(a))

The condensation reaction of DMAn and the carboxyl groups of pAc was carried out as follows. First, 2 wt% of pAc synthesized as described above, DMAn and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) were dissolved in dehydrated DMF. Molar ratios of DMAn and EDC to carboxyl groups in the polymer were fixed at 1.5. Then, the mixture was stirred at 30 °C for 24 h. After the reaction, the resultant solution was poured into acetone to precipitate a polymer. After filtration, the resulting polymer was further purified by reprecipitation from DMF with an excess amount of acetone. DMAn-attached pAc is denoted as pAc-DMAn in the following text.

The deprotection reaction was conducted as follows. First, 0.3 wt% of pAc-DMAn and dehydrated dichloromethane were stirred under a nitrogen atmosphere and cooled to 0 °C. Then, 1 M BBr₃ solution
in dehydrated dichloromethane was added dropwise to the solution. The molar ratio of BBr$_3$ to the polymer unit was greater than 3. The reaction was conducted at 0 °C with stirring for 24 h under nitrogen flow. The polymer precipitated as the reaction proceeded. After the reaction, the solution was allowed to reach room temperature. The precipitated polymer was then filtered and washed with dichloromethane or hexane several times. Next, the resultant polymer was dissolved in water or methanol, and stirred for at least 1 h. Then, the solution was poured into an excess amount of acetone to precipitate the polymer. The deprotected product of pAc-DMAn is denoted as pAcQ in the following text.

Immobilization of Hydroquinone through Alkyl Spacer (phHAQ and pcHAQ, Scheme 1(b))

The condensation reaction of DMAn and phHAc or pcHAc and the subsequent deprotection reaction were carried out under basically the same conditions as those for pAcQ. The differences in reaction conditions are described below. In the condensation reaction, the polymer concentration in the reaction mixture was 3.8 wt%, and 1-hydroxybenzotriazole monohydrate (HOBt) was added to the mixture. The molar ratio of HOBt to carboxyl groups in the polymer was fixed at 1.5. The solvent used to precipitate the polymer was toluene for phHAc. DMAn-attached phHAc and pcHAc are denoted as phHAc-DMAn and pcHAc-DMAn, respectively, in the following text. In the deprotection reaction, the molar ratio of BBr$_3$ to the polymer unit was greater than 4. When the polymer was dissolved in water or methanol after the reaction with BBr$_3$, DMF was added to the solution to fully dissolve the polymer. The deprotected products of phHAc-DMAn and pcHAc-DMAn are denoted as phHAQ and pcHAQ, respectively, in the following text.

Immobilization of Hydroquinone through Di(Ethylene Oxide) Spacer (pEDQ, Scheme 1(c))

The introduction of the di(ethylene oxide) side chain to pAc was typically performed as follows. First, 0.2 g of commercially available pAc (average Mv ca. 450,000) was dissolved in 16 mL of water, and
4.2 mL of EDOA was added to the solution. Then, a mixture of 0.86 g of HOBt, 1.08 g of EDC, and 13 mL of water was added to the solution. The molar ratio of EDOA to the carboxyl groups in pAc was 10, to avoid cross-linking reactions. The reaction mixture was stirred at 30 °C for 24 h, and dialyzed (MWCO 14,000, Sanko Junyaku Co. Ltd, Japan) against H2O at room temperature for 4 days. The purified polymer was then recovered by evaporation.

Immobilization of HQAI was typically carried out as follows. To a solution of 0.04 g of EDOA-attached-pAc and 0.24 g of HQAl in 12 mL of 0.1 M phosphate buffer solution (pH 7.0, PBS), a solution of 0.11 g of NaCNBH3 in 8 mL of 0.1 M PBS was added. The reaction mixture was stirred at 30 °C for 24 h and dialyzed against H2O at room temperature for 3 days. The purified polymer was then recovered by evaporation. The final product in scheme 1(c) is denoted as pEDQ in the following text.

**Detailed Experimental Procedures for Graft Polymerization and Immobilization of the Hydroquinone to the Grafted Polymer**

The introduction of alcoholic hydroxyl groups onto a carbon black surface was achieved as follows. First, 1.5 g of carbon black, 45 mL of formaldehyde aqueous solution, and 0.46 g of sodium hydroxide were placed in a flask. After 5 min of supersonic treatment, the mixture was heated to 70 °C and stirred for 24 h. The resulting carbon black was filtered and washed with water and ethanol several times.

Graft polymerization of AAc onto the carbon black was typically carried out as follows. A mixture of 0.3 g of carbon black containing alcoholic hydroxyl groups, 0.15 g of AAc, and 9 mL of water was placed in a flask. After deaeration of the mixture under vacuum and by bubbling nitrogen gas through it, 1.0 mL of 0.2 mol/L solution of ceric ammonium nitrate in 1 mol/L nitric acid was added. The polymerization was conducted at 35 °C with stirring for 24 h. After the reaction was complete, the resulting carbon black was filtered, extracted with water using a Soxhlet apparatus over a period of 20 h to remove monomer and ungrafted polymer completely, and dried in vacuo at 50 °C for 8 h.

Introduction of di(ethylene oxide) side chain to the grafted polymer was typically conducted as
follows. To a mixture of 0.2 g of pAc-grafted carbon black, 7 mL of water, and 2.6 mL of EDOA, a solution of 0.53 g of HOBt and 0.67 g of EDC in 13 mL of water was added. The reaction was carried out at 30 °C with stirring for 24 h. The resulting carbon black was filtered, extracted with water using a Soxhlet apparatus over a period of 12 h, and dried in vacuo at 50 °C for 8 h.

Immobilization of HQAl was typically carried out as follows. To a mixture of 0.1 g of carbon black with grafted pAc with di(ethylene oxide) side chains, 0.12 g of HQAl, and 6 mL of 0.1 M PBS, a solution of 0.055 g of NaCNBH₃ in 6 mL of 0.1 M PBS, was added. The reaction was carried out at 30 °C with stirring for 24 h. The resulting carbon black was filtered, extracted with water using a Soxhlet apparatus over a period of 12 h, and dried in vacuo at 50 °C for 8 h.
Results and Discussions

Spectrochemical Characterization of Hydroquinone-Immobilized Linear Polymers via Various Spacers

Figure S1 shows FT-IR spectra of the final products in scheme 1, pAcQ (a), phHAQ (b), and pEDQ (c). The peaks at 1650 cm\(^{-1}\) and 1540 cm\(^{-1}\), caused by amide I and amide II bands, respectively, were observed in all spectra. The peaks caused by out-of-plane aromatic C–H bending at 870 cm\(^{-1}\) and 810 cm\(^{-1}\) were obtained in pAcQ (a) and phHAQ (b), and a small peak at 810 cm\(^{-1}\) was observed in pEDQ (c). The pEDQ (c) had a peak at 1110 cm\(^{-1}\), which is a characteristic peak of C–O–C asymmetric stretching vibration of aliphatic ethers. Compared with the spectra of pAc-DMA and phHAc-DMA (data not shown), peaks caused by C–O–C symmetric and asymmetric stretching vibration of alkyl aryl ether at 1040 cm\(^{-1}\) and 1280 cm\(^{-1}\), respectively, disappeared after the deprotection reaction (pAcQ (a) and phHAQ (b)). The FT-IR spectrum of pcHAQ was almost the same as that of phHAQ (data not shown).

Figure S1 FT-IR spectra of (a) pAcQ, (b) phHAQ, and (c) pEDQ. Arrows in the figure show peaks mentioned in the text.
Figure S2 shows NMR spectra of pAcQ (a), phHAQ (b), and pEDQ (c). Peaks caused by aliphatic protons of the polymer backbone between 1 and 2 ppm and by aromatic protons of hydroquinone at 6.3 and 6.7 ppm in pAcQ (a) and phHAQ (b), and at 6.6 ppm in pEDQ (c), were observed in all spectra. The phHAQ (b) had peaks caused by the alkyl spacer between 1 and 3 ppm, as reported previously, part of which overlapped the polymer backbone. Characteristic peaks caused by the di(ethylene oxide) spacer were obtained in pEDQ (c) between 3.0 and 3.6 ppm. A methoxy proton signal at 3.67 ppm, which was observed in the spectra of pAc-DMAn and phHAc-DMAn (data not shown), completely disappeared after the deprotection reaction (pAcQ (a) and phHAQ (b)). The NMR spectrum of pcHAQ, was almost the same as that of phHAQ (data not shown).

These FT-IR and NMR spectra showed the successful synthesis of pAcQ, phHAQ, pcHAQ, and pEDQ.

The degree of modification was defined as the molar ratio of hydroquinone to polymer backbone and was determined from $^1$H NMR spectra by comparing the integration of the aromatic protons of hydroquinone with the integration of aliphatic protons of polymer backbone for pAcQ and pEDQ and with the integration of aliphatic protons of polymer backbone and alkyl spacer for phHAQ. For pcHAQ,
before the determination of the degree of modification, the molar ratio of AmHAc to AAm was
determined by comparing the integration of methylene protons adjacent to the carbonyl group on the
free or hydroquinone-immobilized end, occurring at 2.2 ppm, with the integration of aliphatic protons of
the polymer backbone and spacers, occurring between 1 and 2 ppm. The degrees of modification of
pAcQ, phHAQ, pcHAQ, and pEDQ were about 10, 60, 30, and 3 mol%, respectively.

References

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1757.