Supporting information for:

Nitroxide polymer networks formed by Michael addition: on site-cured electrode-active organic coating†

Takeshi Ibe,[a] Rainer B. Frings,[b] Artur Lachowicz,[b] Soichi Kyo,[a] and Hiroyuki Nishide*[a]

[a] Department of Applied Chemistry, Waseda University, 169-8555 Tokyo, Japan.
[b] DIC Berlin GmbH R&D Laboratory, 13403 Berlin, Germany.
Fax: +81(0)3 3209 5522; Tel: +81(0)3 3200 2669; E-mail: nishide@waseda.jp

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1. Materials and Synthetic Procedure

Materials. All solvents, trimethylolpropane triacrylate (TMPTA), and pentaerythritol tetraacrylate (PETA) were purified by distillation prior to use. A glassy carbon (GC) substrate was purchased from Nilaco Co. A carbon fiber felt was purchased from Nippon Carbon Co., Ltd. Tetrabutylammonium perchlorate ($(C_4H_9)_4NClO_4$) and 4-hydroxy-2,2,6,6-tetramethyl-piperidinyl-*N*-oxyl were obtained from Tokyo Kasei Co. and purified by recrystallization. All other regents were obtained from Sigma-Aldrich Inc.

Preparation of 2,2,6,6-tetramethylpiperidinyl-*N*-oxyl-4-yl acetoacetate (TEMPO-AcAc). To a toluene solution (50 mL) of *tert*-butyl acetoacetate (8.27 g, 52.3 mmol) was added 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-*N*-oxyl (9.00 g, 52.3 mmol), and the mixture was stirred at 100ºC for 15 h. After evaporation, the mixture was purified by silica gel column chromatography with a acetone/petroleum ether (1/3) eluent to afford 2,2,6,6-tetramethylpiperidinyl-*N*-oxyl-4-yl acetoacetate as a red oil (7.38 g, yield 55%). The nitroxide radical group was characterized by the *g*-value (2.0058) of the ESR signal in dichloromethane solution, which was in agreement with that of TEMPO. The radical concentration (100%) was determined by the integrated ESR intensity with that of the solution of TEMPO as the standard. The product was chemically reduced with ascorbic acid to measure the ^{1}H and ^{13}C NMR spectra. IR (cm^{-1}): 1731 ($\nu_{C=O}$); ^{1}H NMR: δ = 5.18 (m, 1H, COOCH), 3.45 (s, 2H, $COCH_2CO$), 2.29 (s, 3H, $COCH_3$), 1.97 (d, 2H, CH_2), 1.58 (d, 2H, CH_2), 1.26 (d, 12H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz; ppm): δ = 207.0 ($COCH_3$), 166.6 (CH_2CO), 70.0 ($OCHCH_2$), 67.5 ($COCH_2CO$), 60.4 ($NC(CH_3)_2$), 43.3 ($OCHCH_2$), 31.0 ($C(CH_3)_2$), 30.3 ($COCH_3$), 20.5 ($C(CH_3)_2$); MS *m/z* = 256.15 (calcd.), 256 (found).

Formation of the nitroxide radical networks. The nitroxide radical networks were formed by mixing TEMPO-AcAc with either TMPTA or PETA at a 1:1 stoichiometric ratio of acrylates to acidic protons of acetoacetate. Briefly, appropriate amounts of each reactant were vigorously mixed with 1 wt% of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in a sample vial, resulting in a viscous fluid due to proceeding reaction. The sample was coated on a Teflon plate with a film applicator. The liquid coating with a thickness of *ca.* 100 μm was then placed at room temperature for 24 h. For each system, gelation was observed visually with a few minutes of mixing. The film was postcured at 80ºC for 2 h, to yield a solid red film of the nitroxide radical

network.

Polymer characterization. The radical concentrations were determined by means of SQUID measurement using the Curie plots. Gel fraction analysis was performed using acetone for 3 days followed by drying in a vacuum oven for 12 h at 40ºC. Dynamic mechanical measurements were conducted on a TA Instruments Q-800 DMA at a heating rate of 2ºC min^{-1} at 1 Hz frequency in film-tension mode.

Electrode preparation. The nitroxide radical networks on GC substrate were also formed by mixing TEMPO-AcAc with either TMPTA or PETA at a 1:1 stoichiometric ratio of acrylates to acidic protons. An appropriate amount of toluene solution (50 vol%) of each reactant were mixed with 1 wt% of DBU in a sample vial at room temperature. The sample was placed for a few min (for example, 30 min for TEMPO-AcAc/TMPTA, 10 min for TEMPO-AcAc/PETA) to increase the viscosity of the solution. The viscous solution was coated on a GC substrate with a bar coater No. 3. The liquid coating was then placed at room temperature for 24 h to remove toluene and to cure. The coating was postcured at 80ºC for 2 h, to yield a solid red film of the nitroxide radical network with a thickness of *ca.* 10 μm on the GC substrate.

Preparation of TEMPO-AcAc/TMPTA-coated carbon-felt. The nitroxide radical networks on GC substrate were also formed by mixing TEMPO-AcAc with either TMPTA or PETA at a 1:1 stoichiometric ratio of acrylates to acidic protons. An appropriate amount of toluene solution of each reactant were mixed with 1 wt% of DBU in a sample vial at room temperature. A piece of the felt (1.0 x 1.0 x 0.2 cm^3) was soaked in the solution for a few seconds, and placed at room temperature for 24 h to remove toluene and to cure (for example, the monomer solution of 10 vol% concentration allowed 23 mg of coating on 25 mg carbon fiber felt). The felt was heated at 80ºC for 2 h, to yield the polymer-coated felt, in which the weight of the loaded polymer increased with the concentration of the monomer solution.

2. Pictures of the Thermally-Cured Nitroxide Polymers

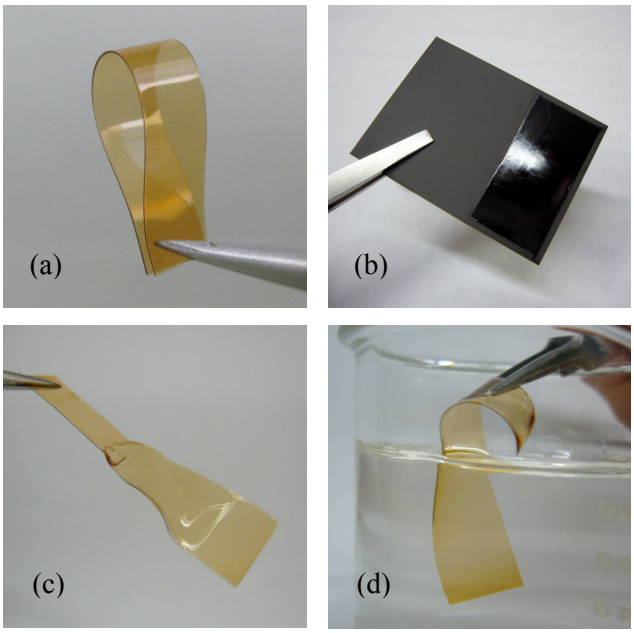

Figure S1. Typical materials of the cured TEMPO-AcAc/TMPTA formed by Michael addition. (a) a bendable and self-standing film with *ca.* 100 μm thickness, (b) a polymer-coated GC substrate with the polymer thickness of *ca.* 10 μm, (c) a film lower-half swollen with CH_3CN, (d) a soft film swollen by soaking in CH_3CN.

3. IR Kinetics Experiments

Kinetic analysis of the Michael addition was performed using IR spectroscopy on JASCO FT/IR-6100 Spectrometer. An appropriate amount of the blend of TEMPO-AcAc with TMPTA, at a 1:1 stoichiometric ratio of acrylates to acidic protons, were vigorously mixed with 1 wt% of DBU in a sample vial. Briefly, the sample was coated on NaCl plate. IR spectra were recorded at regular intervals and the conversion was reported as the ratio of the acryloyl C=C stretch band (1631 cm^{-1}) integration relative to the initial integration, based on the C–H band (2978 cm^{-1}) as an internal reference. The kinetics of DBU-catalyzed Michael reaction was dependent on the concentration. The consumption of the acrylate group detected by IR spectroscopy, in which the band area attributed to the acryloyl C=C stretch at 1631 cm^{-1}, followed pseudo-first-order kinetics (k_{obs} = 5.1 x 10^{-4} s^{-1} at room temperature) at early stage of reaction, due to the equilibrium concentration of the rapidly established enolate ion.

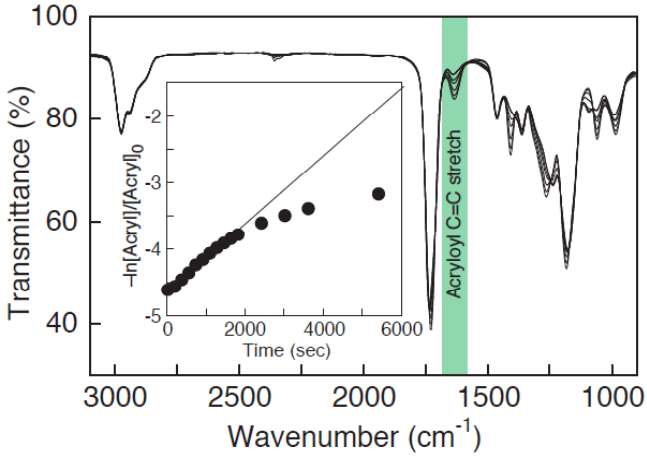

Figure S2. The time course of IR spectra for TEMPO-AcAc/TMPTA crosslinking experiment using 1 wt% DBU, at 0–80000 sec. Inset: First-order rate analysis of acrylate concentration [Acryl] from IR spectroscopy.

4. Electrochemical Study

The electrochemical measurements were performed using a half-cell. A normal potentiostat system (BAS Inc. ALS660C) was used for the cyclic voltammetry, chronopotentiometry and other electrochemical measurements. The nitroxide radical polymer-coated GC substrate, platinum mesh, and Ag/AgCl were used as the working, auxiliary, and reference electrode, respectively. Cyclic voltammogram and the charge/discharge characteristics of the cell was measured in an acetonitrile solution in the presence of 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. The formal potential of the ferrocene/ferrocenium redox couple was 0.45 V vs Ag/AgCl reference electrode.

The diffusion coefficient for the charge propagation within the layer was estimated by chronoamperometry. The slope of the Cottrell plots, which showed linearity under the semi-infinite diffusion conditions (Figure S3), yielded D = 5.2 x 10^{-9} for TEMPO-AcAc/TMPTA and 2.6 x 10^{-9} cm^2 s^{-1} for TEMPO-AcAc/PETA.

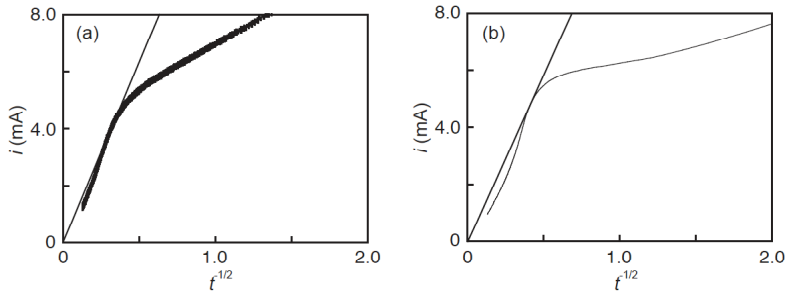

Figure S3. Cottrell curve for chronoamperometry for (a) TEMPO-AcAc/TMPTA and (b) TEMPO-AcAc/PETA film with 10 μm thickness on the GC plate after applying a potential pulse of 0 to 1.2 V vs Ag/AgCl. The solid line corresponds to a semi-infinite diffusion process.

The cyclic voltammetry using the half-cell of the cured TEMPO-AcAc/TMPTA-coated carbon fiber felt was also performed (Figure S4). The redox capacity of the coating polymer were almost in agreement with the capacity calculated with the weight of the polymer. The redox capacity was proportional to the weight, indicating that the TEMPO group of the coating polymer quantitatively worked as the redox site. These results suggested that the thermally-cured TEMPO-AcAc/TMPTA homogeneously coated the carbon fiber felt, and was not dissolving out during the redox reaction.

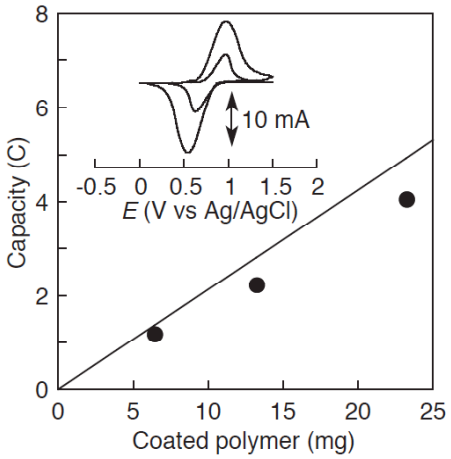

Figure S4. Plots of the redox capacity coulometrically estimated from the cyclic voltammgram at 1 mV s^{-1} scan rate versus the weight of the coated TEMPO-AcAc/TMPTA on 25 mg of the carbon fiber felt electrode. The solid line represents the calculated redox capacity with the weight of the coated polymer. Inset: Cyclic voltammograms of the coated polymer with different amount of coating (23.2 and 6.4 mg) on the carbon fiber felt electrode at 1 mV s^{-1} scan rate.