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Anode-Selective Coating of Titanium (IV) Oxide (TiO$_2$) Using Electrophoretic Sulfone-Containing Click Polyester

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ABSTRACT: We synthesized, at room temperature, aliphatic (**1**-**4**) and aromatic (**5**-**8**) poly(ester-sulfide)s, via a thiol-ene click polymerization of bis(pentenyl)methylsuccinate (BPMSA) and bis(pentenyl)phthalate (BPPh), respectively, with several dithiol including 1,2-ethanedithiol (EtDt), 1,3-propanedithiol (PrDt), 1,4-butanedithiol (BuDt), and 1,5-pentanedithiol (PeDt)   ($M_n = 0.7\text{-}5.2 \times 10^4$, $M_w/M_n = 1.6\text{-}2.6$). Subsequent Oxone oxidation of poly(BPPh-*alt*-BuDt) (**7**), as an example, led to the corresponding poly(ester-sulfone) **7**' ($M_n = 30,000$, $M_w/M_n = 1.8$). We then pepared a composite of **7**' and TiO$_2$ by using elecrophoretic deposition (EPD). The TiO$_2$/poly (ester-sulfone) **7**' composite was selectively deposited onto a stainless-steel anode. The electrode's morphology was confirmed by scanning electron microscopy. We characterized the relationship between the structure of the composite-coated electrode and the zeta potential of an *N,N*-dimethylformamide/alcohol suspension of poly (ester-sulfone) **7**'. The measured values, –(33.27–18.3) mV, indicate that the composite had indeed been selectively deposited on the anode. Notable, from the suspention with the negative potential of –33.27 mV, the thickest composite film was obtained. Furthermore, photo-catalytic activity occurred on the surface of the composite when immersed in aqueous rhodamine-B for 1 month.

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INTRODUCTION

Titanium dioxide (TiO_2) is used in a wide range of applications including as a photocatalyst, printing photoconductor, catalyst support, and solar-battery component. In particular, numerous investigations and patents have been published concerning TiO_2 as a photocatalyst because, to date, only TiO_2 has been found to have practical applications.[1–5] Among the major findings, one group that is particularly important, is that the photocatalytic activity of TiO_2 depends strongly on its morphology (surface area),[6–8] crystal phase,[9–11] and efficient use of light energy.[12,13] Electrophoretic coating of TiO_2 onto a variety of metal surfaces is a promising approach for frontier material studies and applications (smart coating). Several investigations have reported on the elecrophoretic deposition (EPD) of TiO_2 nanoparticles using organic suspensions[14a–14c] or mixtures of organic solvents and water[14d–14g], but there has been no previous work, to the authors' knowledge, on the anode (+) selective EPD of TiO_2. Instead, the EPD of TiO_2 nanoparticles without the addition of stabilizers and using water–ethanol mixtures has been achieved at low voltages.[14h] Also, the EPD of TiO_2 without bubble formation has been possible by using mixed water–alcohol suspensions with the addition of compounds such as $(C_2H_5)_4NOH$ and Tiron molecule,[14i,14j] in which addition of ethanol reduces the zeta potential but prevents water electrolysis. The preparation of TiO_2 coatings from aqueous suspensions with the addition of stabilizers such as carboxylic acids and NaOH has also been reported.[14h] Recently, Boccaccini et al. reported the preparation of TiO_2 coatings from suspensions of TiO_2 nanoparticles in water without the addition of organic stabilizers has been achieved by not direct current (DC) but alternating current (AC) electrophoretic deposion (AC-EPD).[14i] In the all reports, TiO_2 deposited on the cathode, because the nanoparticles of TiO_2 acquired a positive surface charge at pH ca. 4 and the zeta potential of these TiO_2 nanoparticles in water has been documented in the literature.[14j]
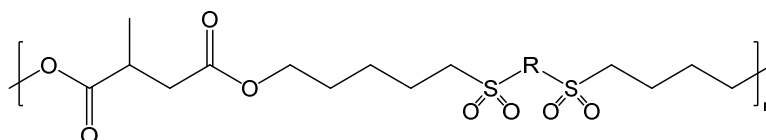
Methylsuccinic acid (MSA)-based (BPMSA-containing) aliphatic poly(ester-sulfone)s (**1-4**)

1: R=EtDt, **2**: R=PrDt, **3**: R= BuDt, **4**: R=PeDt
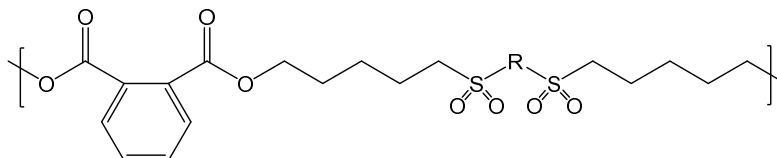
Phthalic acid (PA)-based (BPPh-containing) aromatic poly(ester-sulfone)s (**5-8**)

5: R=EtDt, **6**: R=PrDt, **7**: R= BuDt, **8**: R=PeDt

R: derived from following dithiol monomers

1,2-ethanedithiol (EtDt)　　　　　1,3-propanedithiol (PrDt)

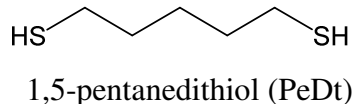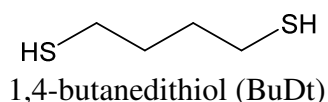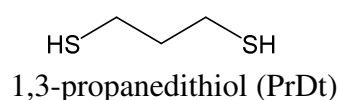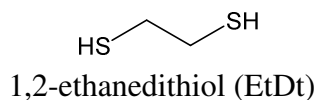1,4-butanedithiol (BuDt)　　　　　1,5-pentanedithiol (PeDt)

Figure 1. Chemical structures of aliphatic (**1-4**) and aromatic (**5-8**) poly(ester-sulfone)s used for this study.

Polyesters are interesting candidates for use as coating materials, because of their excellent physical, mechanical, and bioactive properties,[15] which are usually produced by condensation of a diol and a dicarboxylic acid or a hydroxylcarboxylic acid,[16] or by ring-opening polymerization of a lactone.[17] The former method requires severe reaction conditions even when a customized catalyst is used,[18] and the latter uses highly strained cyclic monomers, which makes it difficult to synthesize polyesters with specific functionalities and/or properties. During this decade, we have reported on low-temperature polycondensations of diols and dicarboxylic acids,[19] which allowed us to use thermally labile monomers that contain functional groups,[20] in which we could not observe electrophoretic behavior of the functional polyesters.　On the other hand, click chemistry, introduced by Sharpless and co-workers,[21-23]

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has been shown to be an efficient tool for the preparation of a wide range of organic compounds. We have also reported on the syntheses of polyesters that contain main-chain triazole units by Cu(I)-catalyzed click polymerization of dialkynes and diazides[24a,24b] and sulfide-containing polyesters by thiol-ene click[25] polymerization.[24c] Recently, we unexpectedly found a series of electrophoretic nonionic poly(ester-sulfone)s **1'-4'** (Figure 1) prepared via oxidation of a series of bis(pentenyl) methylsuccinate (BPMSA)-containing poly(esters-sulfide), poly(BPMSA-*alt*-dithiols) **1-4** (Figure 1), via thiol-ene click polymerization of BPMSA with dithiols and subsequent oxidation,[24c] in which we demonstrated anode-selective coating of a bioactive glass, 45S5 bioglass, on the stainless steel by electrophoretic deposition (EPD). Given the electrical characteristics of sulfones, i.e., electrochemical stability, oxidation potential, and ionic conductivity, we could then selectively deposit the composite onto a stainless steel anode by EPD.
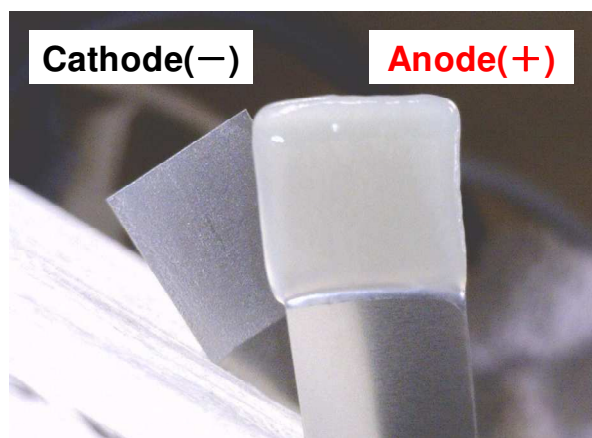
Figure 2. Anode-selective electrophoretic deposition of the TiO$_2$/ poly(ester-sulfone) **7'** (Table 1, entry7).

EPD is a useful technique for the fabrication of inorganic and organic films[26] and involves the controlled electric–field-induced deposition of charged particles or molecules onto a metal electrode. Nano- to micrometer-thick films of organic/inorganic composites can be prepared using EPD in an expected thickness of the films,[26] in which the thickness was easily controlled by electronic current and voltage, electrophoretic time.

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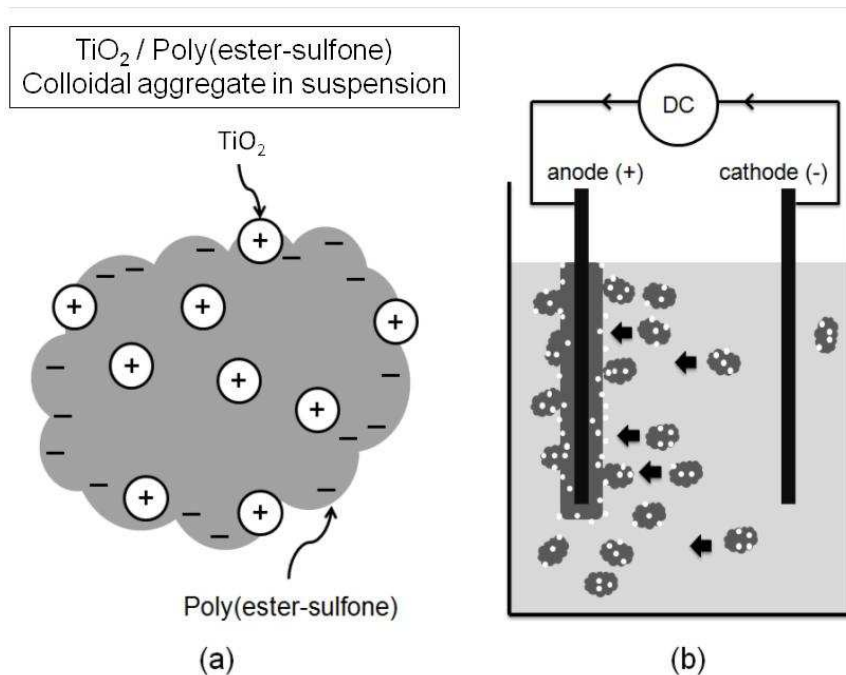**Figure 3.** (a) Schematic of a charged TiO$_2$/poly(ester-sulfone) colloid in an organic solvent (gray background). (b) Schematic of an electrophoretically controlled deposition of the TiO$_2$/poly(ester-sulfone) colloid onto a stainless steal anode.

These research background prompted us to explore anode selective coating of TiO$_2$ particle (Figures 2 and 3). For this article, we demonstrate that aliphatic (**1**-**4**) and aromatic (**5**-**8**) poly(ester-sulfone)s can form a composite with titanium (IV) oxide (TiO$_2$), thereby providing a self-cleaning material for EPD. Finally, we demonstrate the photo-catalytic activity of the composite-coated by aromatic (**5**-**8**) poly(ester-sulfone)s when immersed in aqueous rhodamine-B and compare its activity with that coated by the aliphatic poly(ester-sulfone) (**1**-**4**).

EXPERIMENTAL SECTION

Materials and Methods. Chemicals were obtained from commercial sources and used without further purification. ^{1}H-NMR spectra were acquired at 27°C using a Bruker Analytik DPX200 spectrometer (200 MHz). Tetramethylsilane was the internal standard (0 ppm). The FT-IR spectrum of each poly(esters-sulfone) in a KBr disk wasobtained using a JASCO/IR-430 spectrometer. Number average molecular weights (M_n) and polydispersity indexes (M_w/M_n) for the polyesters were measured

using a size exclusion chromatography (SEC) system consisting of a Tosoh DP8020 pump system, a Tosoh RI-8020 differential refractometer, and Tosoh TSK-gel α-3000 and α-5000 columns (Tosoh, Tokyo, Japan). The eluent was 0.05% (w/v) LiBr, 100 mM tetramethylethylenediamine in *N,N*-dimethylformamide (DMF). The flow rate was 0.5 mL/min, and the temperature was 40°C. Dynamic light scattering (DLS) measurements were performed using a system equipped with an ALV/SO-SIPD detector and an ALV-7002 correlator. Particle size was measured at a 90°-scattering angle and at 30°C. A He-Ne laser (λ = 632.8 nm; NEOARK NEO-30MS2) was used as the light source. For the DLS measurements, 20 μL of each composite emulsion [poly(ester-sulfone) **7'** (in DMF:*n*-BuOH (2/2, v/v) emulsion) was diluted with 10 mL H_2O. The obtained auto-correlation function was analyzed by CONTIN program, and the second-order cumulant method was then used to evaluate the variance μ_2/Γ^2. Particle size distribution was defined as $1 + \mu_2/\Gamma^2$, which approximately corresponds to the M_w/M_n. The Γ value was transformed into the hydrodynamic radius (R_h) by the Einstein-Stoles equation. Zeta potential measurements were performed using a Zetasizer Nano ZS (Malvern Instruments, UK). Mesurement principle was Electrophoretic Light Scattering.

Preparation of Bis(pentenyl)phthalate (BPPh). Phthalic acid (2.5 g, 15 mmol), bis(nonafluorobutanesulfonyl)imide (87 mg, 0.15 mmol), and 4-penten-1-ol (5.167 g, 60 mmol) were added into a 50-mL round-bottom flask. The mixture was stirred at 90°C for 18 h under reduced pressure (90 mmHg), then diluted with 30 mL chloroform, washed with 30 mL of saturated $NaHCO_{3(aq)}$, and dried over $MgSO_4$. After filtration and solvent evaporation, bis(pentenyl)phthalate (BPPh) was obtained as a white liquid in 78% yield (3.5 g). ^{1}H-NMR (200 MHz, $CDCl_3$, δ): 7.78–7.67, 7.59–7.48 (m, O=CC$_6$*H$_4$*C=O, 4H), 5.96–5.70 (m, C=C*H*CH$_2$, 2H), 5.14–4.96 (m, C*H$_2$*=C, 4H), 4.38–4.25 (t, CH$_2$C*H$_2$*OC=O, 4H, 6.5 Hz), 2.19 (m, C=CHC*H$_2$*CH$_2$, 4H), 1.84 (q, CH$_2$C*H$_2$*CH$_2$OC=O, 4H, 6.9 Hz).

Synthesis of the Aromatic Poly(ester-sulfide)s 5-8 (Table 1, entry 5–8) by Photo-Polymerization. A series of 10-mL round-bottom flasks were prepared that each contained BPPh (1.0 mmol), 1-hydroxycyclohexyl phenyl ketone (Irgacure 184; 2.0×10^{-2} mmol), and 1,2-ethanedithiol (EtDt),

1,3-propanedithiol (PrDt), 1,4-butanedithiol (BuDt), or 1,5-pentanedithiol (PeDt) (1.0 mmol each) in 1 mL of distilled toluene. The mixtures were each stirred at room temperature under nitrogen and UV-irradiated using a Toshiba H-400P high-pressure mercury lamp (400 W; and −400 nm) for various times. Then the mixtures were individually diluted with $CHCl_3$. The poly(ester-sulfide)s were individually precipitated twice from $CHCl_3$ by addition of n-hexane and dried under vacuum. White syrups were obtained. Details for the syntheses are summarized in Table 1. The polymer preparations were characterized by ^{1}H-NMR spectroscopy and SEC. ^{1}H-NMR (200 MHz, $CDCl_3$, δ): **5**, 7.84–7.70, 7.66–7.53 (m, O=CC$_6$$H_4$C=O, 4H), 4.36 (t, CH$_2CH_2$OC=O, 4H, 6.5 Hz), 2.82-2.56 (m, SCH_2CH$_2$S, 4H), 2.62 (t, CH$_2$CH$_2$CH_2S, 4H, 7.0Hz), 1.95-1.25 (m, O=COCH$_2$CH_2CH$_2$CH$_2$ 4H, O=COCH$_2$CH$_2$CH_2CH$_2$, 4H, O=COCH$_2$CH$_2$CH$_2$CH_2, 4H); **6**, 7.77–7.65, 7.59–7.46 (m, O=CC$_6$$H_4$C=O, 4H), 4.30 (t, CH$_2CH_2$OC=O, 4H, 4.6 Hz), 2.60 (t, CH$_2$CH$_2$SCH_2CH$_2$S, 4H, 7.3 Hz), 2.52 (t, CH$_2$CH_2SCH$_2$CH$_2$S, 4H, 7.2 Hz), 1.92–1.40 (m, O=COCH$_2$CH_2CH$_2$CH$_2$, 4H, O=COCH$_2$CH$_2$CH_2CH$_2$, 4H, O=COCH$_2$CH$_2$CH$_2$CH_2, 4H, SCH$_2$CH_2CH$_2$S, 2H)**; 7**, 7.76–7.65, 7.59–7.46 (m, O=CC$_6$$H_4$C=O, 4H), 4.30 (t, CH$_2CH_2$OC=O, 4H, 6.6Hz), 2.58-2.42 (m, CH$_2$CH_2SCH_2CH$_2$, 8H), 1.90-1.40 (m, O=COCH$_2$CH_2CH$_2$CH$_2$, 4H, O=COCH$_2$CH$_2$CH_2CH$_2$, 4H, O=COCH$_2$CH$_2$CH$_2$CH_2, 4H, SCH$_2$CH_2CH$_2$CH$_2$S, 4H)**; 8**, 7.77–7.62, 7.59–7.44 (m, O=CC$_6$$H_4$C=O, 4H), 4.30 (t, CH$_2CH_2$OC=O, 4H, 6.6 Hz), 2.50 (m, CH$_2$CH_2SCH_2CH$_2$, 8H, 7.0 Hz), 1.84–1.34 (m, O=COCH$_2$CH_2CH$_2$CH$_2$, 4H, O=COCH$_2$CH$_2$CH_2CH$_2$, 4H, O=COCH$_2$CH$_2$CH$_2$CH_2, 4H, SCH$_2$CH_2CH$_2$CH$_2$CH$_2$S, 4H, SCH$_2$CH$_2$CH_2CH$_2$CH$_2$S, 2H).

    Oxone Oxidation of the Poly(ester-sulfide)s (1-8) to Poly(ester-sulfone)s (1'-8'). An example (Table 1, entry 5) of the oxidation of the poly(ester-sulfide) to the poly(ester-sulfone) follows. Aromatic poly(ester-sulfide) **5** (500 mg, 1.2 mmol repeating unit) and Oxone (1.4 g, 2.2 mmol) in DMF (8 mL) were added into a 30-mL round-bottom flask. After stirring at 70°C for 6 h, the mixture was filtered, and the solvent was evaporated under reduced pressure to give a white solid that was then dissolved in 5 mL of DMF and precipitated by addition of 90 mL H_2O. A total of 471 mg of the poly(ester-sulfone) was obtained as a white solid. The product was characterized by ^{1}H-NMR spectroscopy and SEC. The

conversion of the sulfide into the sulfone was calculated using the ^{1}H-NMR intensity ratio of the signals at 4.23 ppm (CH$_2$CH_2OC=O) and 3.27 ppm (CH$_2$CH$_2$CH_2SO$_2$CH_2) for **5'**; or 3.31–3.06 ppm (m, CH$_2$CH_2SO$_2$CH_2CH$_2$, 8H) for **6'**; or 3.21–2.99 ppm (m, CH$_2$CH_2SO$_2$CH_2CH$_2$, 8H) for **7'**; or 3.10–2.95 ppm (m, CH$_2$CH_2SO$_2$CH_2CH$_2$, 8H) for **8'**. ^{1}H-NMR (200 MHz, DMSO-d_6, δ): **5´**, 7.78–7.58 (m, O=CC$_6$$H_4$C=O, 4H), 4.23 (t, CH$_2CH_2$OC=O, 4H, 6.1 Hz), 3.51 (s, SO$_2$CH_2CH$_2$SO$_2$, 4H), 3.27 (t, CH$_2$CH$_2$CH_2SO$_2$, 4H, 7.4 Hz), 1.85–1.60 (m, O=COCH$_2$CH_2CH$_2$CH$_2$, 4H, O=COCH$_2$CH$_2$CH$_2$CH_2, 4H), 1.56-1.34 (m, O=COCH$_2$CH$_2$CH_2CH$_2$, 4H); **6´**, 7.70–7.62 (m, O=CC$_6$$H_4$C=O, 4H), 4.23 (t, CH$_2CH_2$OC=O, 4H, 6.1 Hz), 3.24 (t, CH$_2$CH$_2$SO$_2$CH_2CH$_2$SO$_2$, 4H, 7.1 Hz), 3.15 (t, CH$_2$CH_2SO$_2$CH$_2$CH$_2$SO$_2$, 4H, 8.2 Hz), 2.21–1.98 (m, SO$_2$CH$_2$CH_2CH$_2$SO$_2$, 2H), 1.84–1.60 (m, O=COCH$_2$CH_2CH$_2$CH$_2$, 4H, O=COCH$_2$CH$_2$CH$_2$CH_2, 4H), 1.58–1.36 (m, O=COCH$_2$CH$_2$CH_2CH$_2$, 4H); **7´**, 7.79–7.61 (m, O=CC$_6$$H_4$C=O, 4H), 4.24 (t, CH$_2CH_2$OC=O, 4H, 5.5 Hz), 3.21–2.99 (m, CH$_2$CH_2SO$_2$CH_2CH$_2$, 8H), 1.88–160 (m, O=COCH$_2$CH_2CH$_2$CH$_2$, 4H, O=COCH$_2$CH$_2$CH$_2$CH_2, 4H, SO$_2$CH$_2$CH_2CH$_2$CH$_2$SO$_2$, 4H) 1.57–1.36 (m, O=COCH$_2$CH$_2$CH_2CH$_2$, 4H); **8´**, 7.74–7.53 (m, O=CC$_6$$H_4$C=O, 4H), 4.19 (t, CH$_2CH_2$OC=O, 4H, 5.9 Hz), 3.10–2.95 (m, CH$_2$CH_2SO$_2$CH_2CH$_2$, 8H), 1.78–1.54 (m, O=COCH$_2$CH_2CH$_2$CH$_2$, 4H, O=COCH$_2$CH$_2$CH$_2$CH_2, 4H, SO$_2$CH$_2$CH_2CH$_2$CH$_2$CH$_2$SO$_2$, 4H) 1.54–1.32 (m, O=COCH$_2$CH$_2$CH_2CH$_2$, 4H, SO$_2$CH$_2$CH$_2$CH_2CH$_2$CH$_2$SO$_2$, 2H).

Preparation of Stainless Steel Electrodes Coated with TiO$_2$/Poly(ester-sulfone) Composites. TiO$_2$ (anatase crystal) powder of mean particle size <25 nm was purchased from Sigma-Aldrich and used without additional purification. A suspension of TiO$_2$ in 7.5 mL of ethanol and 7.5 mL of H$_2$O$_2$ was agitated in an ultrasonicator (BRANSONIC® Yamato 2510) for 15 min and then stirred for 5 min. Each poly(ester-sulfone) was stirred in 15 mL of DMF for 15 min at 60°C to obtain a homogeneous solution. Then the TiO$_2$ and each poly(ester-sulfone) solution were individually mixed, ultrasonically agitated for 15 minutes, and then stirred for 5 min. For deposition of each TiO$_2$/poly(ester-sulfone) composite onto a 0.2 × 15 × 25 mm stainless steel SUS 301 electrode (The Japan Metal Service Corporation, Saitama, Japan) by EPD, the distance between the electrodes was 7.5 mm and the deposition time was 30–90 s at

a current of 2–6 mA. The poly(ester-sulfone)s, prior to EPD and recovered from the electrode after EPD, were characterized by ^{1}H-NMR and FT-IR spectroscopy, and by scanning electron microscopy (SEM) (dual-stage JSM-6010LA microscope; JEOL Ltd., Tokyo, Japan).

Photo-catalytic activity of TiO₂/Poly(ester-sulfone) on Composite Films. The ability of the composites to photo-catalyse was investigated by their immersion of composite films in aqueous rhodamine-B (10^{-5} M). After holding each sample in the solution for 120 minutes under UV (250–400 nm) irradiation, each composite was removed and dried. The solution was characterized by UV, fluorescence measurement, additionally the composite film was characterized by ^{1}H-NMR and SEC.

RESULTS AND DISCUSSION

Syntheses of Sulfone-containing aromatic polyesters. According to our procedure for the synthesis of the poly(ester-sulfone),[24c] we first attempted to individually prepare sulfide-containing aliphatic polyesters (**1-4**) by thiol-ene photo-polymerization of BPMSA with different dithiols and with Irgacure 184 as the photo-initiator, under UV irradiation, at room temperature (Scheme 1 and Table 1 entries 1-4). Polymerization proceeded rapidly even under air. Polymerization at 25°C proceded and was complete within several hours. Within 15–30 min, each photo-polymerization gave an aliphatic poly(ester-sulfide) of large M_n in good to excellent yields (84-95%, Table 1, entry 1-4). The SEC data demonstrated that the poly(ester-sulfide)s have M_w/M_n values 1.6–2.4 that are commonly found for ordinary A-A- and B-B-type step-growth polymerizations.[25]

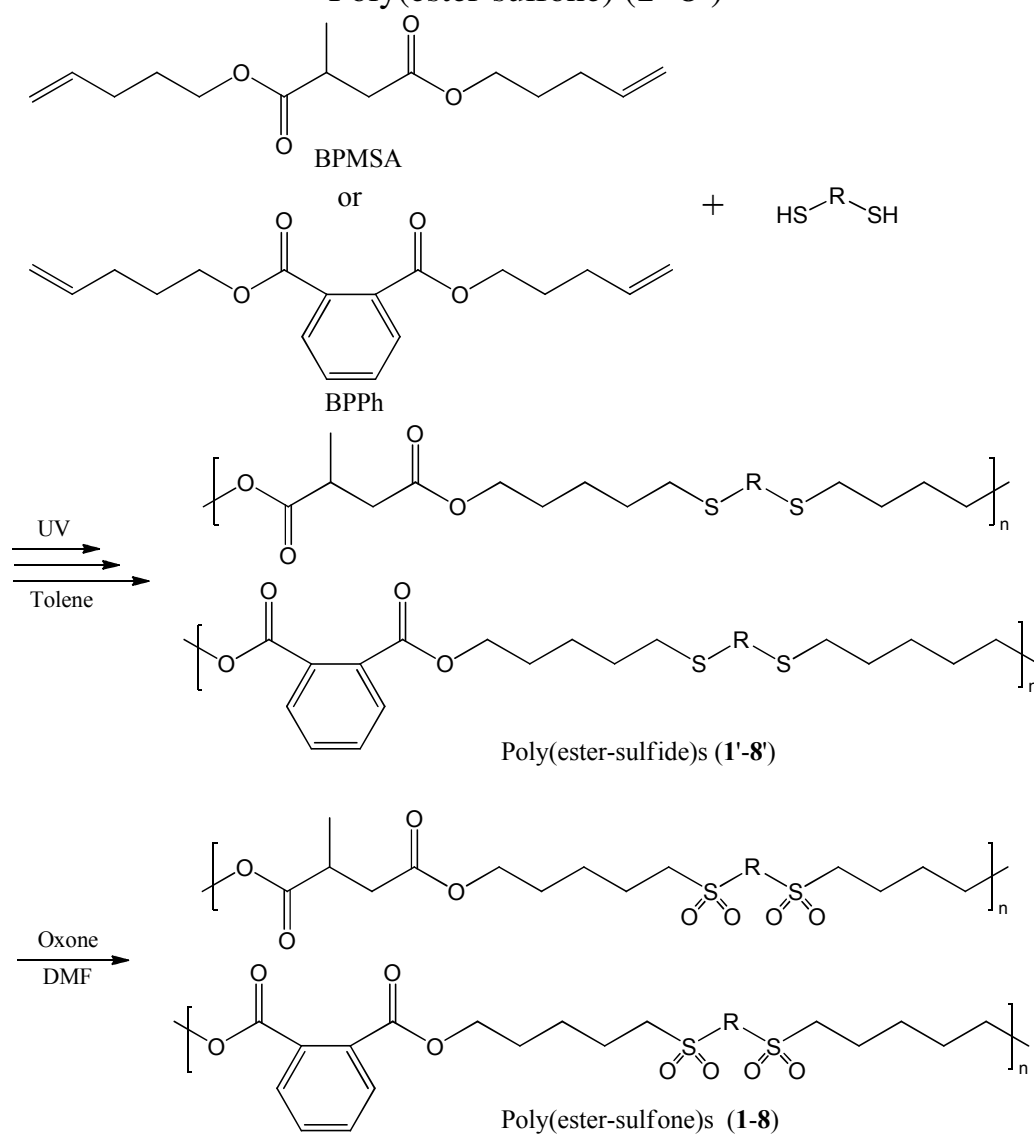**Scheme 1.** Synthesis of Poly(ester-sulfide) (**1**-**8**) and Subsequent Oxone Oxidation to Poly(ester-sulfone) (**1'-8'**)

BPMSA

or

+ HS—R—SH

BPPh

UV / Tolene

Poly(ester-sulfide)s (**1'-8'**)

Oxone / DMF

Poly(ester-sulfone)s (**1-8**)

Table 1. Poly(ester-sulfide)s and Poly(ester-sulfone)s Synthesized for This Study

entry	ester-containing dialkene	dithiol	poly(ester-sulfide)[a]			poly(ester-sulfone)[c]		
				$M_n{}^b$ ($\times 10^4$)	$M_w/M_n{}^b$		conv.[d] (%)	$M_n{}^b$ ($\times 10^4$)	$M_w/M_n{}^b$
1	BPMSA	EtDt	**1**	5.2	1.6	**1'**	95	3.1	1.9
2	BPMSA	PrDt	**2**	2.9	2.4	**2'**	91	1.4	1.8
3	BPMSA	BuDt	**3**	3.4	2.6	**3'**	84	2.8	2.3
4	BPMSA	PeDt	**4**	1.0	2.0	**4'**	95	1.0	1.8
5	BPPh	EtDt	**5**	0.7	1.8	**5'**	>99	1.0	1.4
6	BPPh	PrDt	**6**	0.9	1.8	**6'**	>99	1.3	1.5
7	BPPh	BuDt	**7**	2.4	2.4	**7'**	90	3.0	1.8
8	BPPh	PeDt	**8**	1.0	1.8	**8'**	98	1.0	1.8

[a] Prepared by thiol-ene click polymerization of ester-containing dialkenes (BPMSA and BPPh) and dtithiols at room temperature (25 °C) in the presence of Irgacure using UV irradiation. [b] Determined by SEC mesurement in DMF relative to poly(styrene) standards. [c] Prepared by Oxone oxidation.of the parent poly(ester-sulfide) in DMF at 70 °C for 6h. [d] Determined by ^{1}H NMR.

Additionally, we conducted photo-initiated thiol-ene polymerizations of BPPh and dithiol monomers to produce aromatic poly(ester-sulfone)s (Sheme 1 and entries 5-8 in Table 1). When EtDt and PrDt were used as monomers, the reactions did not produce poly(ester-sulfide)s of large M_ns and good yields (Table 1, entries 5,6). These poly(ester-sulfide)s would have a short methylene chain between the thiols, and we considered that the steric hindrance between the aromatic units restricted the molecular motion of the poly(ester-sulfide) main chain or that the aromatic ring that absorbs UV light, which inhibit the reactions.[22] When we used BuDt as the dithiol, the corresponding poly(ester-sulfide), poly(BPPh-*alt*-BuDt) (**7**), with M_n of 2.4 x 10^4 was synthesized.

Next, we investigated the Oxone oxidation of the poly(ester-sulfide)s **1**-**8** to produce the corresponding poly(ester-sulfone)s. (Table 1, entries 1-8) According to our reported procedure,[24c] 2 equiv. of Oxone per sulfide quantitatively converted the sulfides to the sulfones. IR absorbance bands (1070–1030 cm^{-1}) ascribable to sulfoxides (the reaction intermediate) were not observed and neither were any ^{1}H-NMR resonances that would be associated with a sulfoxide. However, IR absorbancies at 1271 cm^{-1} and 1124 cm^{-1}, characteristic of sulfones, were present. The M_ns of the poly(ester-sulfone)s **1'**-**8'** (sulfonation conversion = 100%) was similar to that of its parent poly(ester-sulfide)s **1**-**8**. For

example (run 4, Table 1), M_n of poly(ester-sulfide) **4'** (1.0×10^4) was similar to that (1.0×10^4) of the parent poly(ester-sulfide) **4**. Moreover, the M_w/M_ns for the two polyesters were similar (1.8 and 2.0 respectively), indicating that neither degradation nor side reactions occurred during the oxidation.

Electrophoretic Deposition of TiO₂/Poly(ester-sulfone) Coatings. In the case of a bioactive glass, ethanol, rather than *n*-butanol, more effectively controlled the stability of the suspension of aliphatic poly(ester-sulfone)s **1'-4'**.[24c] Therefore, we selected a film prepared from the DMF/ethanol mixture and the results are summarized in Table 2. Mixtures of TiO₂ and a poly(ester-sulfone)s **5'-8'** (Table 1, entries 5-8) actually formed colloidal suspensions in DMF/*n*-butanol as well as DMF/ethanol, and could be deposited onto a stainless-steel anode by EPD. Notably, virgin TiO₂ particles moved towards the cathode (Table 2, entry 1) because these particles are positive charged in mild acidity solutions (pH, 6.2).[14i,27] Conversely, we found that not the poly(ester-sulfide)s **1-8** but the poly(ester-sulfone)s **1'-8'** migrated to the anode by virtue of the patially negative charge on the sulfone oxygen, which suggests this charge polarized sulfones dominates the surface charge of the composite. The ¹H NMR spectrum (Figure 4) of the poly(ester-sulfone) **3'** (Table 1, entry 3) before and after deposition onto the electrode indicates that EPD did not alter its structure/composition. Ordinary aliphatic polyesters, e.g., polycaprolactone (prepared in our laboratory, M_n=7,900, M_w/M_n=1.30) or polylactic acid, are not charged either, so that when they are part of a TiO₂ composite, they are EPD deposited onto the cathode (Figure 5), which makes the deposition of the TiO₂/poly(ester-sulfone)s (prepared in Table 1, enyries 5-8) onto the anode an unusual phenomenon. Therefore, the electrophoretic behavior of a TiO₂/polyester composite can probably be controlled by the type of polyester.

Upon examining the TiO₂/poly(ester-sulfone)s **7'** deposited films associated with different EPD conditions, we found cracks in the films prepared from the pure poly(ester-sulfone) **7'** (M_n=1.1x10⁴) suspension (12 g/L; Table 2, entry 2) and in the TiO₂/poly(ester-sulfone) films prepared from the colloidal suspension that contained 6 g poly(ester-sulfone)/L solvent (Table 2, entries 3–8). When we used higher molecular weight poly(ester-sulfone)s **7'** (M_n= 3.0×10^4) using the optimized condition (polymer concentration, 6 g/L), the composite films had cracked. These results indicated that the

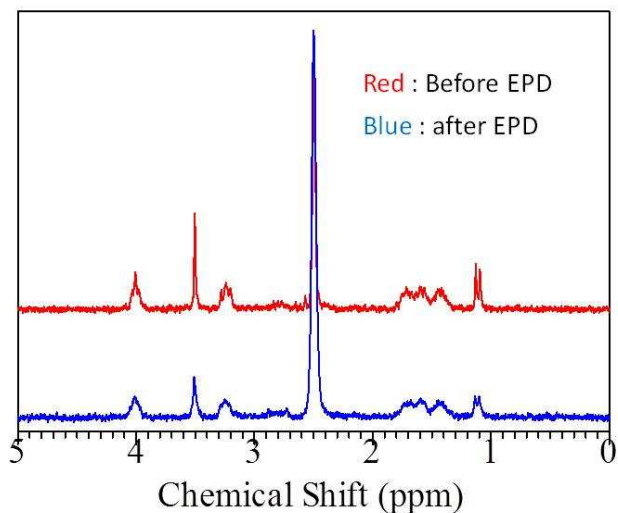molecular weight of poly(ester-sulfone)s **7'** influenced on the EPD coating.

Figure 4. ^{1}H-NMR spectrum of the poly(ester-sulfone) **3'**(Table 1, entry **3**) before EPD (red) and after EPD (blue).
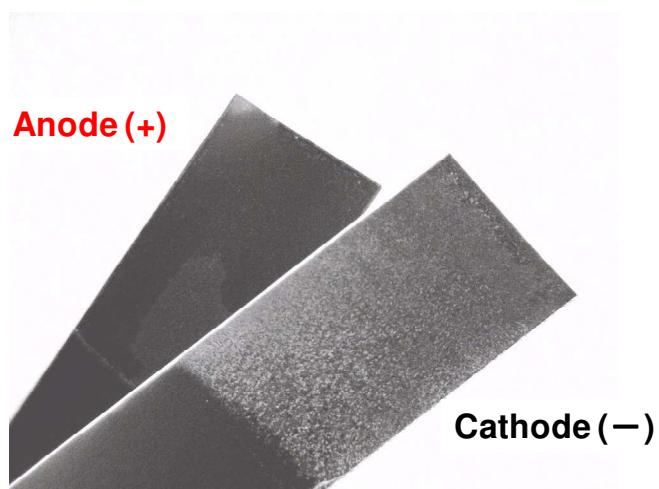

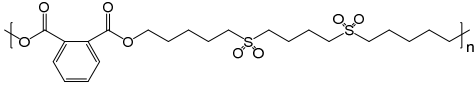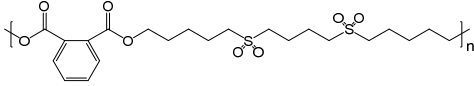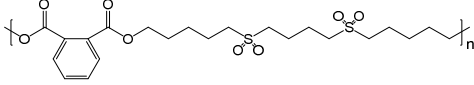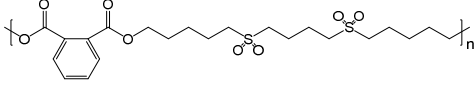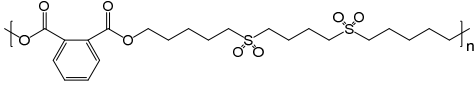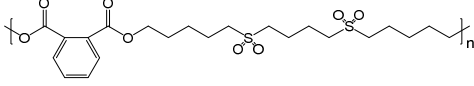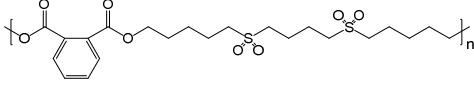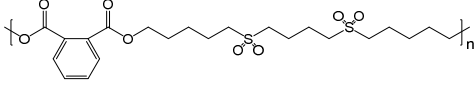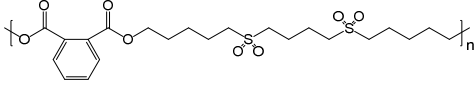**Figure 5.** Cathodic electrophoretic deposition of the TiO_2/ polycaprolactone.

Table 2. TiO$_2$/Poly(ester-sulfone) Coating on the Stainless Steel Electrode by EPD[a]
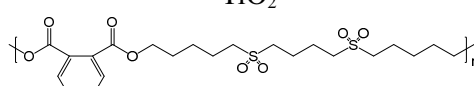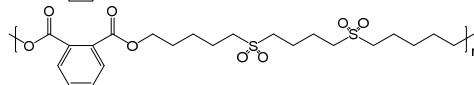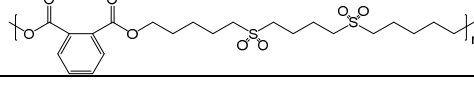
entry	content	poly(ester-sulfone) g/L	M_n^a ($\times 10^4$)	time (sec)	current (mA)	electrode	image of the electrode deposit
1	TiO$_2$	0	—	60	20	cathode	brittle
2		12	1.1	90	4	anode	cracked
3	/TiO$_2$	6	1.1	30	2	anode	thin
4	/TiO$_2$	6	1.1	30	4	anode	thick
5	/TiO$_2$	6	1.1	30	6	anode	thick
6	/TiO$_2$	6	1.1	90	2	anode	thin
7	/TiO$_2$	6	2.2	30	2	anode	thin
8	/TiO$_2$	6	2.2	90	2	anode	thin
9	/TiO$_2$	6	3.0	30	2	anode	cracked
10	/TiO$_2$	6	3.0	90	2	anode	cracked

[a] At a current of 2-6 mA, 30-90 second.   [b]Determined by GPC measurement in DMF relative to poly(styrene)s.

Zeta Potential Measurements of the Poly(ester-sulfone) Emulsions. To characterize the electrophoretic behavior of the TiO$_2$/poly(ester-sulfone) **7**'-covered anodes, its zeta-potential of

poly(ester-sulfone) **7'** was measured in different mixtures of DMF and *n*-butanol (Table 3). The measured negative values (-33.27--18.3 mV) supported the anode selective deposition, and the larger negative values were, the more stable suspensions were obtained.

Table 3. Zeta-Potential Measurements of Suspentions Consisting of Poly(ester-sulfone) 7' in DMF/*n*-BuOH

Entry	Contant	Suspention DMF:*n*-BuOH (v/v)	Zeta potential[a] (mV)	EPD coating
1	TiO$_2$	2:2	1.8	cathode
2		2:2	−33.3	anode
3		3:1	−18.3	anode
4		1:3	0.4	no coating

[a]Determined by Zetasizer Nano ZS.

Dynamic Light Scattering of the Poly(ester-sulfone) 7' Emulsion in the Absence and Presence of TiO$_2$. DLS measurements are also carried out to investigate average particle size of poly(ester-sulfone) **7'** [in DMF:EtOH (2/2, v/v)] emulsions in the absence and presence of TiO$_2$ and their size distributions (Figure 6). From the DLS analysis, bimodal traces consisting of average size (hydrodynamic radius: R_h) of 2 µm and 200 µm were observed in the poly(ester-sulfone) emulsions in the absence of TiO$_2$. In the presence of the TiO$_2$, unimodal trace was observed with peak top of 2 µm, and the particle size distribution is much broader than that in the absence of TiO$_2$ (Figure 6). It seems that the particle size is influence by the TiO$_2$. These results indicated that the emulsion is composed of the seed TiO$_2$ coated with poly(ester-sulfone) as the shell.
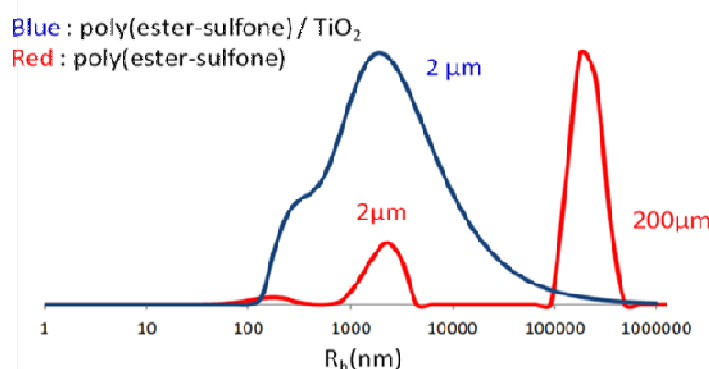
Figure 6. DLS measurements of poly(ester-sulfone) **7'** (in DMF:EtOH (2/2, v/v) emulsions in the absence (red) and presence (blue) of the TiO_2.

Characterization of TiO_2/poly(ester-sulfone) 7' Film Prepared by Electrophoretic Coating.

We assessed the surface and cross-section morphology of the TiO_2/poly(ester-sulfone) **7'** film by SEM and EDX. The SEM images of the film show that TiO_2 particles are well dispersed in a matrix formed by the poly(ester-sulfone) (Figures 7a, 7c). Figures 7b and 7d show a SEM image and an EDX map for the film, respectively. The colors in the EDX map identify carbon (red), titanium (green), and sulfur (blue) and indicate that the TiO_2 particles were homogeneously dispersed, i.e., the poly(ester-sulfone) surrounds and is in close contact with the TiO_2 particles. Our results surely indicate that a TiO_2/poly(ester-sulfone) colloidal diphasic suspension has formed (see Figure 6) and that the sulfone moieties were responsible for anode-selective deposition. The composite thickness was 35 μm on average by cross-section SEM observation, and from the EDX mapping of the cross-section, it looks that population of TiO_2 in the poly(ester-sulfone) **7'** matrix was uniform (data not shown). As to stability of the surface, the surfaces (Figures 7e) and the elements population (Figures 7f) are not changed for 1 month after photo irradiation.
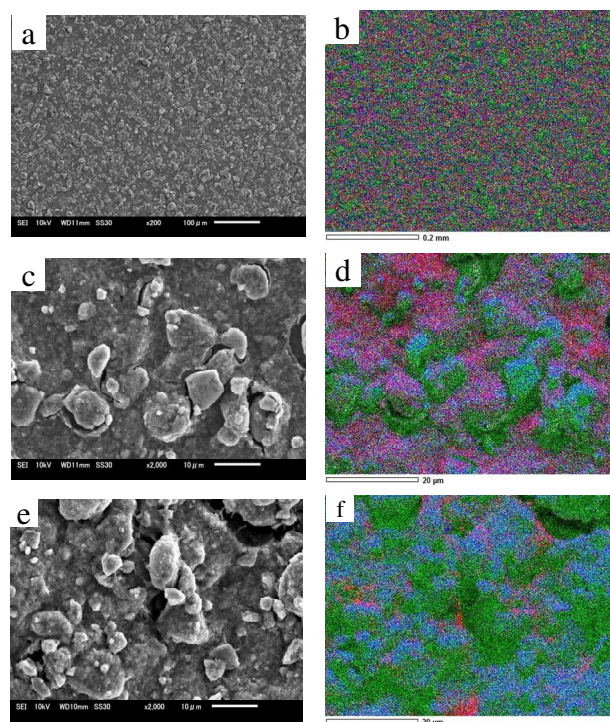
Figure 7. Scanning electron micrographs of TiO_2/Poly(ester-sulfone) **7'** films. Surfaces of the composite a) at low magnification (×200) and c) at high magnification (×2000). b) and d) EDX map, showing the distribution of carbon (red), titanium (green), and oxygen (blue), of the composite (×200, ×2000

magnification). e) and f) Same surface of upper ones for 1 month after photocatalystic activity test.
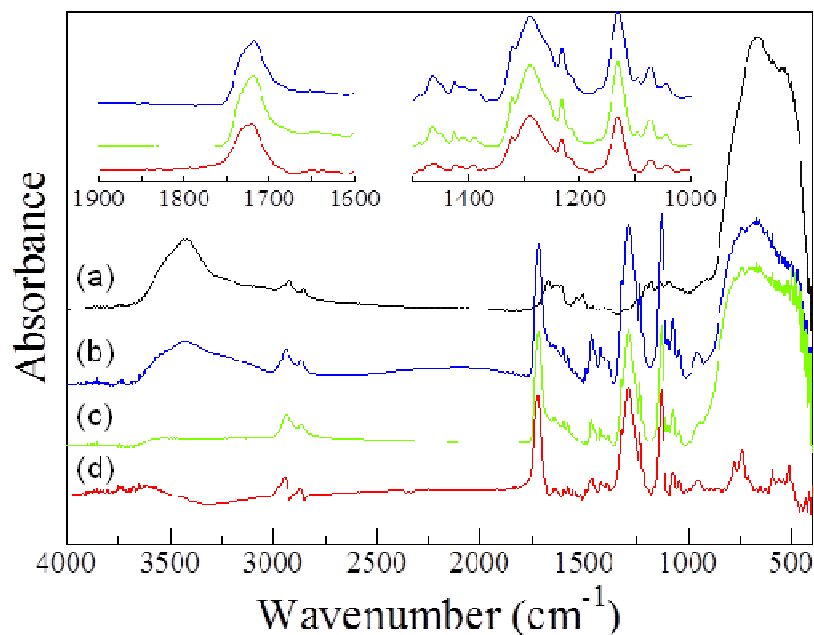
Figure 8. FT-IR spectra of (a) pure TiO_2, (b) TiO_2/poly(ester-sulfone) **7'** physical mixture, (c) TiO_2/poly(ester-sulfone) EPD coating, (d) pure poly(ester-sulfone) **7'**.

In the IR spectrum of TiO_2/poly(ester-sulfone) after EPD coating, signal ascribed to TiO_2 apeared at 1600 cm^{-1} and 668 cm^{-1}, which coincided with those of the parent TiO_2 (at 1620 cm^{-1} and 671 cm^{-1}) and broadening of the peak ascribed to poly(ester-sulfone) moiety at 1718 cm^{-1}, 1288 cm^{-1} and 1129 cm^{-1} was not observed. The results indicated that the ligand exchange of TiO_2 and strong coordination to poly(ester-sulfone) did not occur.

Photocatalytic Activity on the Surface of Electrophoretically Deposited TiO_2 / Poly(ester-sulfone) Composites. Photocatalytic activity was confimed on the surface of electorophoretically deposited TiO_2/aliphatic and aromatic poly(ester-sulfone)s (**3'** and **7'**) composites by immersing in 7 mL of $1.0x10^5$ M rhodamine-B aqueous solution (Figure 9). For 120 minutes by UV irradiation, fluorescence of the rhodamine-B aqueous solution disappeared (Figure 9b), indicating self-cleaning ability on the both of aliphatic and aromatic surfaces. However, serious peeling was observed on the TiO_2 / aliphatic poly(ester-sulfone) **3'** (Figure 9c and 9d). On the other hand, the surface of TiO_2 / aromatic poly(ester-sulfone) **7'** was not change compared with that before UV irradiation. In the ^{1}H-NMR spectra (Figure 10, left) and SEC curves (Figure 10, right) of the aromatic

poly(ester-sulfone) **7'** before and after deposition on the electrode (Table 2, entry 8), remarkable changes were not observed either, indicating that photo-degradation of the aromatic poly(ester-sulfone) matrix was not serious during the photoirradiation and the **7'** composite was fixed on the stainless steel even in the aqueous solution.

Aromatic poly(ester-sulfone)

(b)

(a)

Aliphatic polymer surface

(d)

Aliphatic poly(ester-sulfone)

(c)
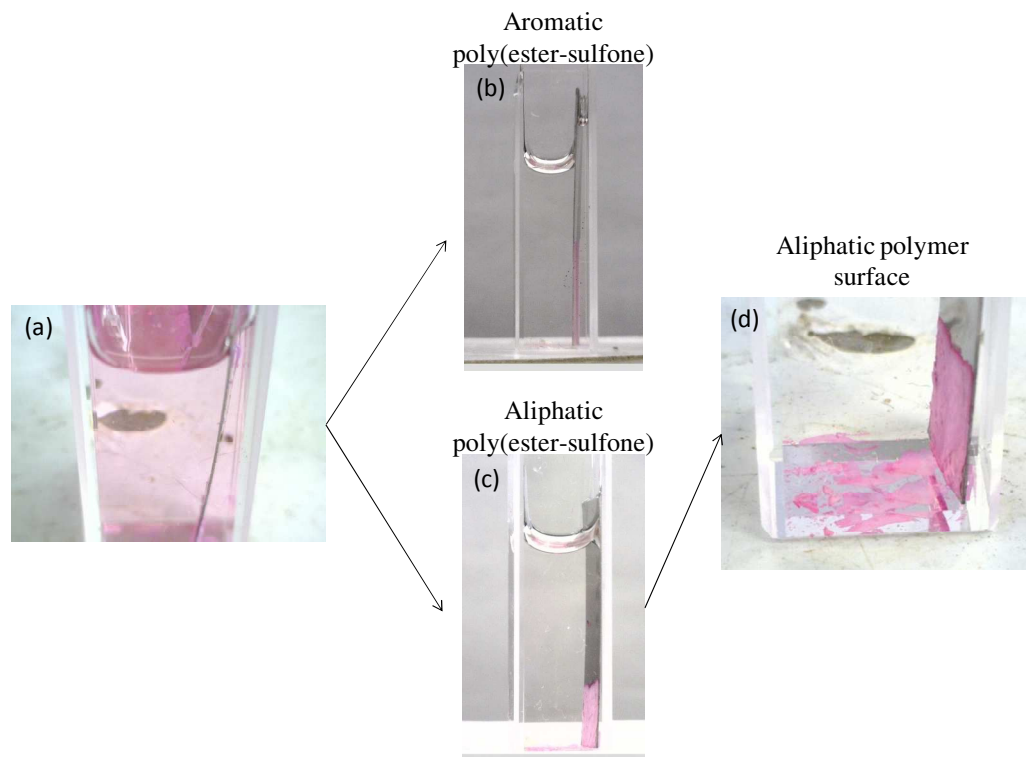
Figure 9. Photographs of TiO$_2$ / aromatic (b) and aliphatic (c) poly(ester-sulfone) (**3'** and **7'**) before (a) and after photo irradiation [(b), (c), and (d)]. The poly(ester-sulfone)s were prepared from the parent poly(ester-sulfide)s **3** and **7**, respectively, and used for the self-cleaning experiments.

Red : Before photo degradation
Blue : After photo degradation

Chemical Shift (ppm)

Red : Before photo degradation
Blue : After photo degradation

Elution Time (min)

Figure 10. ^{1}H-NMR spectra and size exclusion chromatograms of TiO$_2$/poly(ester-sulfone) **7'** composite before and after photo irradiation. The poly(ester-sulfone) **7'** was prepared from the parent poly(ester-sulfide) **7** used for the chromatography.

      The photocatalytic activity using rhodamine-B aqueous solution was also shown in profile of fluorescence intensity ratios of initial fluorescence at 580 nm and that after UV irradiation $[I_{(580)}/I_{0(580)}]$ as a function of time (Figure 11). In both of the previous aliphatic and aromatic poly(ester-sulfone)s (**3'** and **7'**) composites, the $I_{(580)}/I_{0(580)}$ s decreased and the degradation was completed within 120 min. Interestingly, the degradation rate was comparable for that in the presence of the same amount of virgin TiO$_2$. In order to check the difference of the aliphatic and aromatic components, the degradations of rhodamine-B aqueous solution were also carried out in the presence of MSA and PA (see also Figure 11), because the corresponding monomers BPMSA and BPPh are not soluble in the aqueous medium. Unexpectedly, the degradations of rhodamine-B aqueous solution were apparently inhibited in the presence of MSA [MSA /TiO$_2$=1/1, mol/mol; Figure 12, (3)] or PA [PA /TiO$_2$=1/1, mol/mol; Figure 12, (2)], in which the remarkable difference in the degradation behaviors between the aliphatic and aromatic carboxylic acid was not observed. Coordination of the carboxylic acid to TiO$_2$ decreased the catalytic activity, which is well-coinci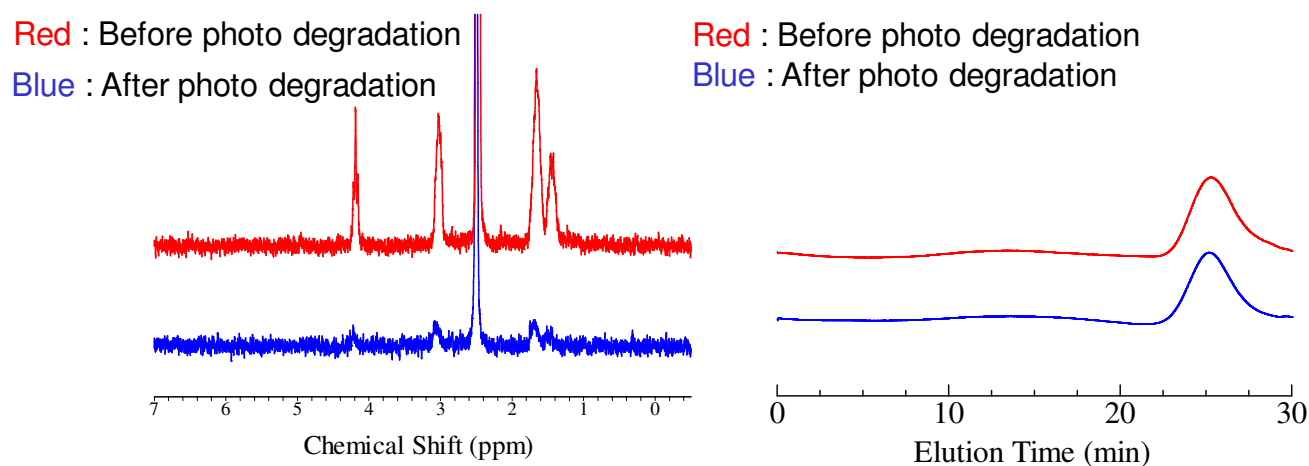ded with reported statement that the treatment with organic modifiers having oxygenated functionalities (hydroxyl or carboxyl groups) in a vicinal position inhibits both reductive and oxidative photocatalytic activity of TiO$_2$.[28] The results strongly supported that it is essential to use nonionic coating materials for coating of TiO$_2$ to fabricate self-cleaning surfaces.
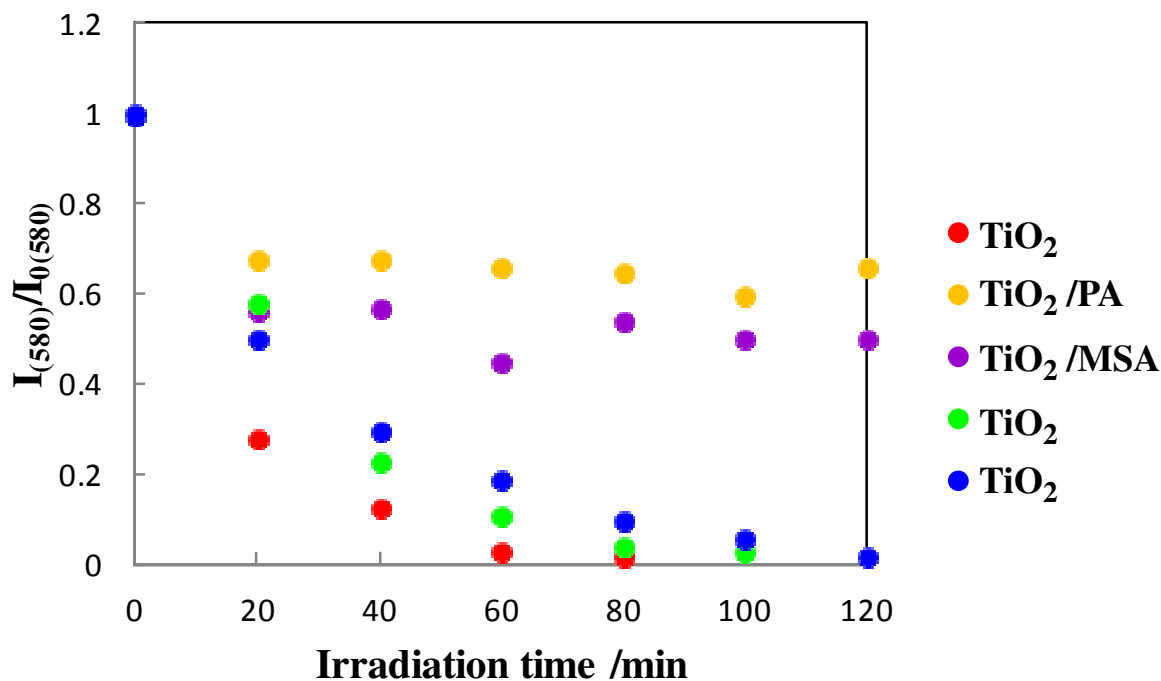
Figure 11. Photodegradation of rhodamine B on the several TiO$_2$ composite, measured by fluorescence spectroscopy.

Figure 12. Investigation of influence of the monomer unit (aliphatic and aromatic carboxylic acids), (1) TiO$_2$, (2) TiO$_2$/phthalic acid (PA), (3) TiO$_2$/methylsuccinic acid (MSA). UV irradiated (a) 0 min, (b) 60 min, (c) 120 min.

After the degradation test, the surfaces of both of aliphatic and aromatic poly(ester-sulfone) (**3'** and **7'**) / TiO$_2$ composites looks red due to the adsorption of rhodamine-B. To the surface, UV irradiation directly performed and after 480 min, the color of the surface turned to be white (Figure 13). The results revealed that the degradation of rhodamine-B surely occurred on the composite surface.

| No UV irradiation | UV irradiation | No UV irradiation | UV irradiation | No UV irradiation | UV irradiation |
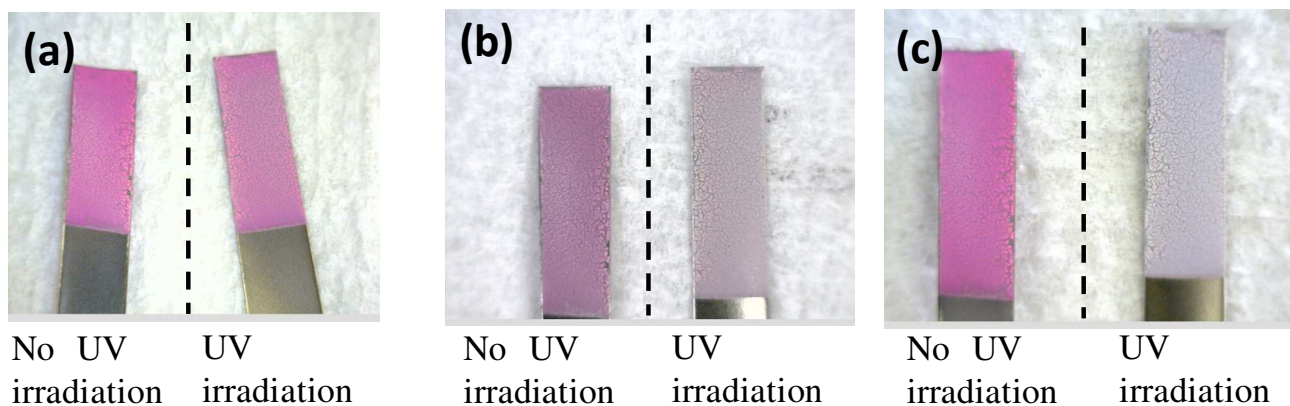
Figure 13. UV irradiated aromatic poly(ester-sulfone) **7'** / TiO$_2$ composites surface (right) in the air for (a) 120 min, (b) 240 min, (c) 480 min.

CONCLUSION

In this study, we prepared a TiO$_2$/click poly(ester-sulfone) colloid, which could be deposited onto a stainless steel surface by EPD to form a soft composite coating. The TiO$_2$/click poly(ester-sulfone) film developed a surface aming at self-cleaning when immersed in rhodamine-B aqueous solution

confirming the photocatalytic activity of the new composite coating. The synthesis of the aromatic poly(ester-sulfone) was facile, and the aromatic poly(ester-sulfone) (**5-8**) were stable in the photo-irradition as well as the EPD condition, e.g. under electric fields, compared with aliphatic poly(ester-sulfone)s (**1-4**). The results reported herein therefore provide a new guideline of smart coating of TiO_2 using electrophoretic coating, aiming at foundation of self-cleaning system.

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Graphical and Textual Abstract
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| **Anode-Selective Coating of Titanium (IV) Oxide (TiO₂) Using Electrophoretic Sulfone-Containing Click Polyester**

Takuya Fukuoka and Akinori Takasu* | |

We synthesized, at room temperature, aliphatic (**1**-**4**) and aromatic (**5**-**8**) poly(ester-sulfide)s, via a thiol-ene click polymerization of bis(pentenyl)methylsuccinate (BPMSA) and bis(pentenyl)phthalate (BPPh), respectively, with several dithiol including 1,2-ethanedithiol (EtDt), 1,3-propanedithiol (PrDt), 1,4-butanedithiol (BuDt), and 1,5-pentanedithiol (PeDt) (M_n = 0.7-5.2 × 10^4, M_w/M_n = 1.6-2.6). Subsequent Oxone oxidation of poly(BPPh-*alt*-BuDt) (**7**), as an example, led to the corresponding poly(ester-sulfone) **7'** (M_n = 30,000, M_w/M_n = 1.8). We then pepared a composite of **7'** and TiO₂ by using elecrophoretic deposition (EPD). The TiO₂/poly (ester-sulfone) **7'** composite was selectively deposited onto a stainless-steel anode. The electrode's morphology was confirmed by scanning electron microscopy. We characterized the relationship between the structure of the composite-coated electrode and the zeta potential of an *N,N*-dimethylformamide/alcohol suspension of poly (ester-sulfone) **7'**. The measured values, –(33.27–18.3) mV, indicate that the composite had indeed been selectively deposited on the anode. Notable, from the suspention with the negative potential of –33.27 mV, the thickest composite film was obtained. Furthermore, photo-catalytic activity occurred on the surface of the composite when immersed in aqueous rhodamine-B for 1 month.