Polymer Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/polymers

A Vinyl Polymer Having Pendent Sulfones Prepared by Atom-Transfer Radical Polymerization of Sulfide-Containing Methacrylate and Electrophoretic Transparent Coating on Stainless-Steel Anode

*Tomomi Kameyama and Akinori Takasu**

Department of Frontier Materials, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

AUTHOR EMAIL ADDRESS: takasu.akinori@nitech.ac.jp

*To whom correspondence should be addressed: Telephone: +81-52-735-7159. Fax: +81-52-735-5342. E-mail takasu.akinori@nitech.ac.jp

ABSTRACT

Sulfide-containing methacrylate was prepared by esterification of methacryloyl chloride with 2-(ethylthio)ethanol. Then Cu(I)-catalyzed atom-transfer radical polymerizations of this methacrylate derivative in toluene was performed or acetonitrile with some ligands for Cu(I). We found that, with toluene as the solvent and 1,1,4,7,10,10-hexamethyltriethylenetetramine as the ligand, the molecular weight of the synthesized polymer was the most controlled ($M_n = 6.7 \times 10^3$, $M_w/M_n = 1.3$). Next, the polymer was oxidized to synthesize a vinyl polymer containing pendent sulfones (oxidation >99%), which was then selectively coated onto a stainless-steel anode by electrophoretic deposition, in which the deposited film was transparent. This last result is consistent with our recent finding that a poly(ester-sulfone), prepared via thiol-ene click polymerization, shows anode-selective deposition behavior.

INTRODUCTION

Electrophoresis is defined as the directionally oriented motion of dispersed particles with a net charge in a fluid under the influence of a spatially uniform electric field.[1-6] This electrokinetic phenomenon was first observed in 1807 by Ferdinand Frederic Reuss (Moscow State University),[7] who noticed that the application of a constant electric field caused clay particles dispersed in water to migrate in one direction. The underlying physicochemical mechanism of electrophoresis involves the presence of a charged interface between the surface of a particle and the surrounding fluid. A variety of biochemical electrophoretic techniques have been widely used for separating macromolecules [e.g., proteins or DNA] by size, charge, and/or binding affinity.[8] Electrophoresis of positively charged particles (cations) is termed cataphoresis, whereas that of negatively charged particles (anions) is termed anaphoresis. However development of electrophoretic separation techniques for permanently polarized molecules is in its infancy; if we could site-specifically introduce polar groups into the structures of macromolecules, we could revolutionize the separation of nonionic polymers via electrophoresis (Figure 1).

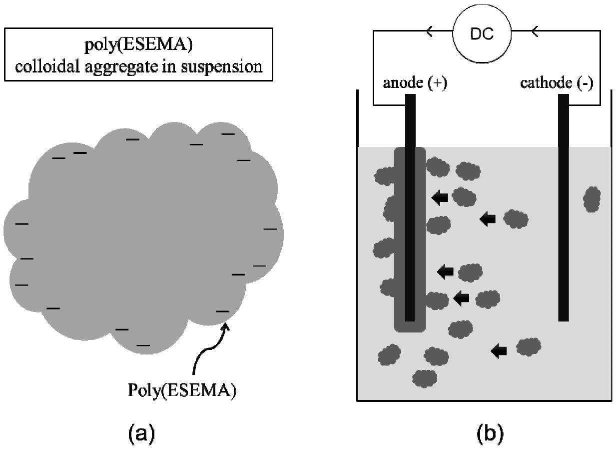
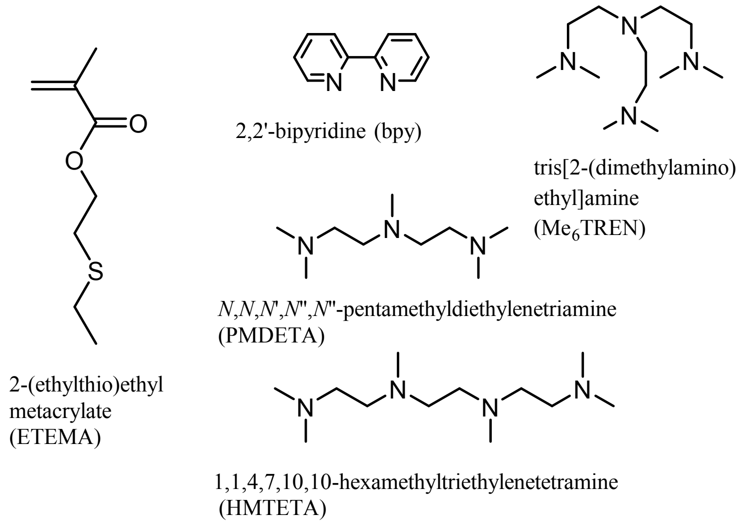


Figure. 1(a) Schematic of poly[2-(ethylsulfonyl)ethyl methacrylate] [poly(ESEMA)] colloid in an organic solvent (gray background). **(b)** Schematic of an electrophoretically controlled deposition of the poly(ESEMA) colloid onto a stainless steal anode.

Design of new materials that can effectively coat a metal substrate at a nano- to micrometer scale is one of the fascinated subjects from the viewpoints of biorelated, energic, and environmental fields.[9] Electrophoretic deposition (EPD) is a promising and facile technique for the fabrication of inorganic or organic or inorganic / organic composite films[9a,10] onto electrode. EPD is based on the controlled electric-field-induced deposition of charged particles or molecules in an orderly manner onto an electrode. The characteristic of EPD is capable of film formation on the complex surface shape, easy to control of thickness and, forming a homogeneous layer.

During the past decade, our group has focused on the development of new synthetic procedures—low temperature polycondensation[11] and click polymerization (polyaddition)—for the preparation of new types of polyesters from ester-containing monomers.[12] Recently, our group found that an aliphatic poly(ester-sulfone) prepared by thiol-ene click polymerization and subsequent oxidation showed anode-selective electrophoresis under EPD conditions.[12c] Anode-selective EPD coatings of bioactive glass (45S5Bioglass)[12c] and titanium dioxide (TiO_2) were also demonstrated.[12d] However, these observations and the interesting electrophoretic behavior of the sulfone-containing polyester prompted us to explore why the poly(ester-sulfone) is deposited onto the anode, and what part of its structure is responsible for this unusual electrophoretic behavior.



2-(ethylthio)ethyl metacrylate (ETEMA)

2,2'-bipyridine (bpy)

tris[2-(dimethylamino) ethyl]amine (Me_6TREN)

N,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine (PMDETA)

1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA)

Figure 2. Chemical structures of the sulfide-containing methacrylate monomer and Cu(I) ligands used in this study.

Therefore, for this report, our group performed Cu(I)-catalyzed atom-transfer radical polymerization (ATRP) of the sulfide-containing methacrylate, i.e., 2-(ethylthio)ethyl methacrylate (ETEMA) and subsequently oxidized the pendant sulfides of the polymer [poly(ETEMA)] (Figure 2) to synthesize the electrophoretic vinyl polymer containing pendent sulfones poly[2-(ethylsulfonyl)ethyl methacrylate] [poly(ESEMA)].[13] We also compared certain properties of the anode-selective electrophoretic coating of poly(ESEMA) with that of the poly(ester-sulfone).[12c] For the latter, its ester and sulfone functionalites are both part of the main chain, whereas for the former, they are part of the side chains. The results reported herein[13] support our recent finding that the poly(ester-sulfone) prepared via thiol-ene click polymerization shows anode-selective deposition behavior.[12c and 12d]

EXPERIMENTAL SECTION

Materials and Methods. 2-(ethylthio)ethanol, methacryloyl chloride 2,2'-Bipyridine (bpy), tris[2-(dimethylamino)ethyl]amine (Me_6TREN), were purchased from Tokyo Chemical Industry (Tokyo, Japan). 2,2'-Azobisisobutyronitrile(AIBN) was purchased from NACALAI TESQUE, INC. (Kyoto, Japan). Ethyl-2-bromoisobutyrarte, 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), *N,N,N′,N′′,N*″-pentamethyldiethylenetriamine (PMDETA), and ethyl-2-bromoisobutyrarte were purchased from Aldrich Chemical Co. (St. Louis, MO, U.S.A.). Triethylamine, dichloromethane, *N,N*-dimethylformamide, and acetonitrile (CH3CN), *n*-butanol (BuOH) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). 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 used as the internal standard (0 ppm). FT-IR spectra of poly(ETEMA) and poly(ESEMA) in KBr disks were obtained using a JASCO/IR-430 spectrometer. The number-average molecular weight (M_n) and the polydispersity index ($M_\mathrm{w}/M_\mathrm{n}$) of each polymer were determined by size exclusion chromatography (SEC) using a Tosoh DP8020 pump system, a refractive index (RI) detector (Tosoh RI-8020), and either a TSKgel SuperMultiporeHZ-M column (eluent, chloroform; flow rate, 0.35 mL/min; temperature, 40 °C; Tosoh Corp.) or using a size exclusion chromatography system consisting of a Tosoh DP8020 pump system, a Tosoh RI-8020 differential refractometer, and Tosoh TSK-gel α-3000 and α-5000 columns [eluent, 0.05% (w/v) LiBr, 100 mM tetramethylethylenediamine in *N,N*-dimethylformamide (DMF); flow rate, 0.5 mL/min; temperature, 40˚C; Tosoh Corp.), in which poly(styrene)s are used as the calibration standard.

Preparation of ETEMA. ETEMA was prepared as follows.[14] 2-(Ethylthio)ethanol

(3.2 mL, 30 mmol), methacryloyl chloride (4.7 mL, 45 mmol), triethylamine (4.6 mL, 45 mmol), dichloromethane (12 mL) were added into a 100-mL round-bottom flask containing a magnetic stir bar. The mixture was stirred at room temperature for 12 h then sequentially washed with $NaOH_{(aq)}$, $KHSO_{4(aq)}$, and saturated $NaCl_{(aq)}$ and then dried over $MgSO_4$. After filtration and subsequent evaporation, ETEMA was obtained as a yellow liquid. After distillation, the monomer was obtained as a colorless liquid in 77% yield. ^1H NMR (200 MHz, $CDCl_3$, δ in ppm): 6.14 and 5.58 (2s, $C\mathit{H}_2$=C(CH_3)C=O, 2H), 4.30 (t, $OC\mathit{H}_2CH_2S$, 2H, 7.6Hz), 2.80 (t, $OCH_2C\mathit{H}_2S$, 2H, 7.6Hz), 2.61 (q, $SC\mathit{H}_2CH_3$, 2H, 7.4Hz), 1.95 [s, CH_2=C($C\mathit{H}_3$)C=O], 1.28 (t, $SCH_2C\mathit{H}_3$, 3H, 7.4Hz) (see also Figure S1)**.**

Synthesis of Poly(ETEMA) by Free Radical Polymerization. ETEMA (1.74 mg, 10 mmol), azobisisobutyronitrile (AIBN) (8.2 mg, 0.05 mmol), distilled toluene (10 mL) were added into a 10-mL round-bottom flask containing a magnetic stir bar. The mixture was stirred at 60˚C under a nitrogen atmosphere for 4 h, at which time unexpected gelation was observed.

Synthesis of Poly(ETEMA) by Atom Transfer Radical Polymerization (ATRP). Polymerization conditions were surveyed, an example follows. ETEMA 0.796 mg(5 mmol), ethyl-2-bromoisobutyrarte 15 μL (0.1 mmol), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) 27 μL (0.1 mmol), CuBr 14 mg (0.1 mmol), and 5 mL of toluene were added to 10 mL round-bottomed flask with a magnetic stir bar in the nitrogen. The mixture was stirred at 60˚C for 96 h, the ATRP proceeded smoothly to give poly(ETEMA) (Table 1, run 3, 79% conversion, $M_\mathrm{n} = 6.7 \times 10^3$, $M_w/M_n = 1.3$). ^{1}H NMR (200 MHz, $CDCl_3$, δ in ppm): 3.96–4.24 (br, $OC\mathit{H}_2CH_2S$, 2H), 2.68–2.85 (brt, $OCH_2C\mathit{H}_2S$, 2H, 7.4 Hz), 2.52–2.68 (brq, $SC\mathit{H}_2CH_3$, 2H, 7.6 Hz), 1.76–2.06 (br, $C\mathit{H}_2CCH_3C{=}O$, 2H), 1.20–1.37 (t, $SCH_2C\mathit{H}_3$, 3H, 7.2 Hz), 1.14 (brs, $CH_2CC\mathit{H}_3C{=}O$, mm), 1.07 (brs, $CH_2CC\mathit{H}_3C{=}O$, mr), 0.92 (brs, $CH_2CC\mathit{H}_3C{=}O$, rr) (see also Figure S2).

Oxone Oxidation of Poly(ETEMA). Oxone (1.94 g, 3.16 mmol) and poly(ETEMA) (549 mg, 3.16 mmol repeating unit) in DMF (21 mL) were added into a 30-mL round-bottom flask containing a stir bar. After stirring at r.t. for 21 h, the mixture was filtered, and the solvent was evaporated under reduced pressure to give a white solid that was then dissolved in DMF (5 mL) and precipitated by addition of 90 mL H_2O. A total of 585 mg of poly(ESEMA) was obtained as a white solid and was characterized by ^{1}H-NMR (Figure S3) and IR (Figure S4) spectra. The extent of the conversion of the sulfide into the sulfone was determined using the intensity ratio of the ^{1}H NMR signals at 2.68–2.85 ($OCH_2C\mathit{H}_2S$) and 3.27–3.50 (m, $OCH_2C\mathit{H}_2SO_2$) ppm. ^{1}H NMR (200 MHz,

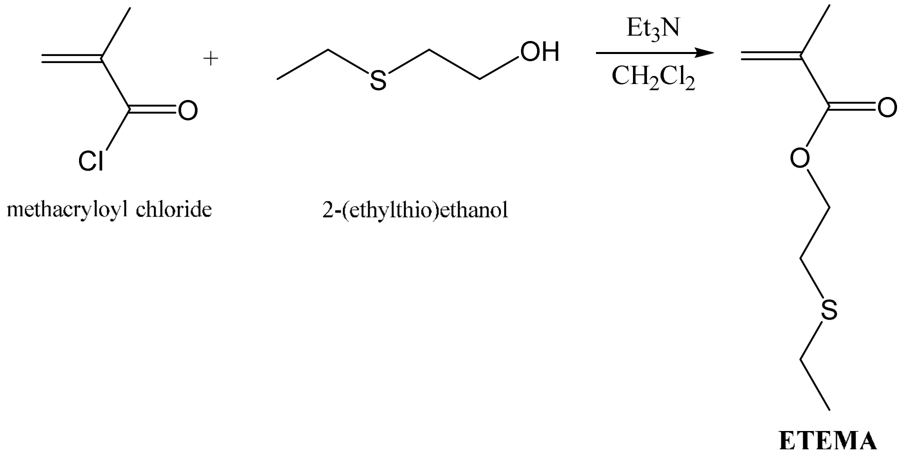
$CDCl_3$, δ in ppm): 4.27–4.52 (m, $OCH_2CH_2SO_2$, 2H), 3.27–3.50 (m, $OCH_2CH_2SO_2$, 2H), 3.03–3.24 (m, $SO_2CH_2CH_3$, 2H), 1.74–2.05 (m, $CH_2C(CH_3)C{=}O$, 2H), 1.36–1.53 (t, $SO_2CH_2CH_3$, 3H, 7.2 Hz), 1.20–1.29 [m, $CH_2C(CH_3)C{=}O$, mm], 0.99–1.17 [m, $CH_2C(CH_3)C{=}O$, mr], 0.79–0.99 (m, $CH_2CCH_3C{=}O$, rr) (see also Figure S3).

Preparation of a Stainless Steel Anode Coated with poly(ESEMA). Poly(ESEMA) (24 mg) was stirred in DMF and DMF/*n*-butanol (BuOH) (4 mL) for 15 min at r.t. to obtain a homogeneous solution and the dispersions, respectively (in a 5 mL of glass bottle). For deposition of poly(ESEMA) onto a stainless steel electrode (0.2 × 15 × 25 mm of stainless steel SUS 301 electrodes, The Japan Metal Service Corporation, Saitama, Japan. The structural component of SUS 301 is iron containing carbon (< 0.15%), sillica (<2.00%), manganese (<2.00%), phosphorus (<0.045%), nickel (6.00 to 8.00%), and chromium (16.00 ~ 18.00%). The distance between the electrodes was 7.5 mm, and the deposition time was 90 s with a current of 1–2 mA. The deposited film was characterized by ^1H-NMR and FT-IR spectroscopy.

RESULTS AND DISCUSSION

Preparation of ETEMA. 2-(Ethyltio)ethanol was reacted with 1.5 eq. of methacryloyl chloride at room temperature for 12 h in the presence of triethylamine, which trapped liberated HCl (Scheme 1). After distillation, the monomer was obtained as a yellow liquid in 77% yield. Its structure was confirmed by ^{1}H-NMR spectroscopy (Figure S1).

Scheme 1. Preparation of ETEMA.



ATRP of ETEMA. It is reported that thioethers are attacked by radicals.[15] We, therefore, had to carefully check the chain-transfer to protect the pendent sulfide moiety. ETEMA undergoes free radical polymerization at 60˚C (initial monomer concentration, 2 M) in the presence of the initiator AIBN to afford a gel. When we decreased the initial monomer concentration to 1 M, gelation still occurred. Therefore, it seems that radicals attacked the pendent sulfides to produce thiyl radicals as the chain-transfer reaction, which initiated the remaining monomers to give branching and subsequent cross-linking (Figure 3).

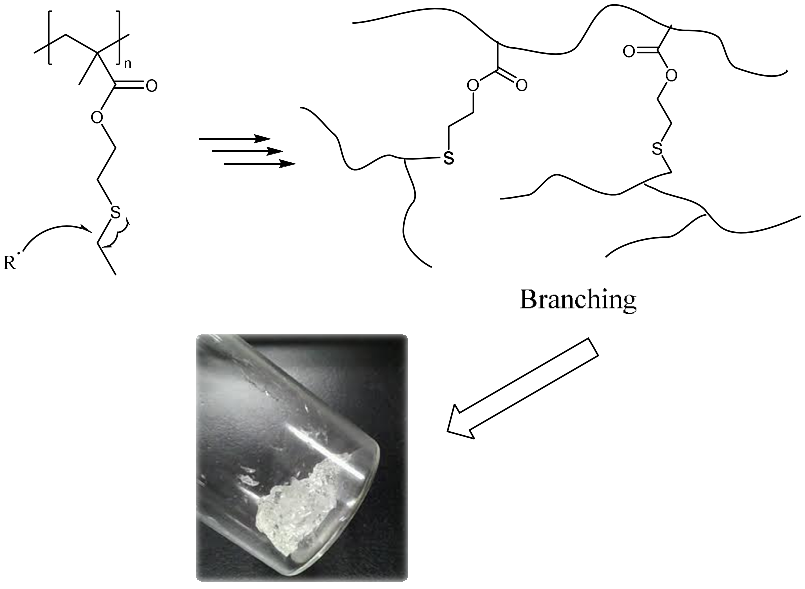
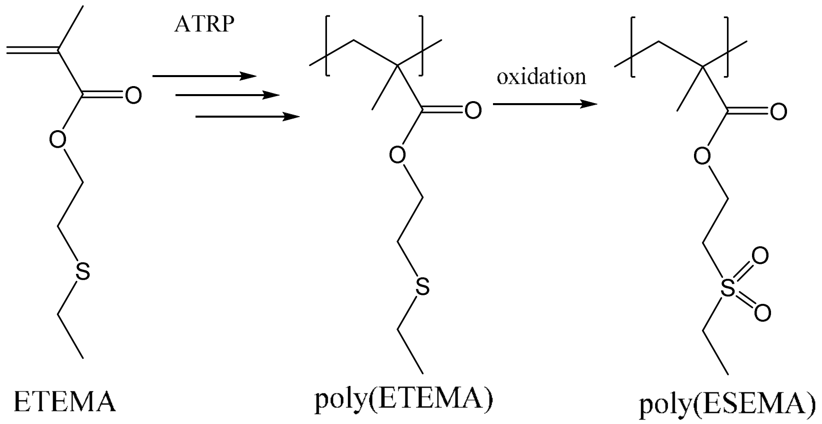


Figure 3. Schematic of free radical polymerization of ETEMA accompanied by branching and cross-linking.

Next, we tried Cu(I)-catalyzed ATRP of ETEMA to suppress the chain transfer as well as to control the molecular weight of poly(ETEMA) by varying the Cu(I) ligand and the solvent (Scheme 2). The results for these experiments are summarized in Table 1. Concerning the Cu(I) ligand, 2,2’-bipyridine (bpy) (runs 1 and 2) or HMTETA (runs 3 and 4) promoted the desired reaction in an expected fashion than did *N,N,N’,N”,N*”-pentamethyldiethylenetriamine (PMDETA) (runs 5 and 6). However, with tris[2-(dimethylamino)ethyl]amine (Me_6TREN) (runs 7 and 8), as the ligand, gelation occurred similar to the free radical polymerization. When we used toluene as the solvent (runs 1, 3, 5, and 7), ATRP proceeded smoothly to give poly(ETEMA) (Table 1, run 3, 79% conversion, $M_n = 6.7 \times 10^3$, $M_w/M_n = 1.3$). The extent of conversion was greater and the molecular weight distribution narrower than when acetonitrile was the solvent (runs 2, 4, 6, 8). In Figure 4, monomer consumption ($\ln([M]_0/[M])$) as a measure of polymer production is plotted as a function of time to characterize how each Cu(I) ligand affected the polymerization rate. A linear dependence for $\ln([M]_0/[M])$ as a function of time at several temperatures was observed with toluene as the solvent and HMTETA or bpy as the ligand. With acetonitrile as the solvent, and HMTETA or PMTETA as the ligand, relatively fast propagation occurred but the reaction ceased at ~2 h, indicating that free radical polymerization and termination caused the accumulation of “dead” polymer molecules. For ATRP in toluene (ligand, HMTEA), the reactivity of the propagating radical seemed to be more readily controlled owing to the presence of a domant species, and we could speculated that the propagating radical did not seem to attack the pendent sulfide moiety. To the best of our knowledge, there are only a few reports dealing with control of a primary structure using ATRP[16] for suppression of branching or cross-linking.

Scheme 2. Synthesis of Poly(ETEMA) and Subsequent Oxidation to Afford Poly(ESEMA).



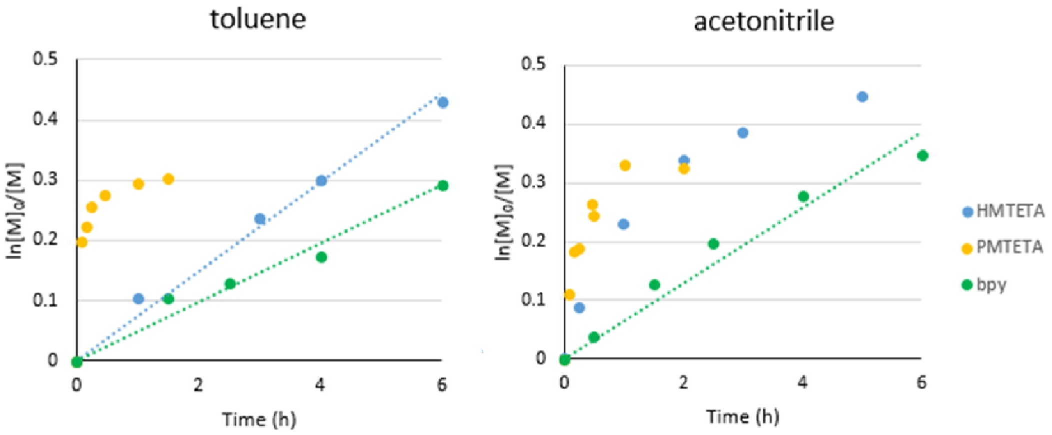


Figure 4. $\ln[M]_0/[M]$ vs. time for ATRP of ETEMA catalyzed by CuBr coordinated with HMTEA (blue circles), PMTETA (orange circles), or bpy (green circles) as the ligand (initiator: ethyl-2-bromoisobutyrarte, $[M]_0 = 1.0$ M).

Table 1. ATRP of ETEMA.[a]

run	ligand	solvent	$M_{\mathrm{n,theo}} \times 10^{-3\,b}$	$M_{\mathrm{n}}{}^{b} \times 10^{-3}$	$M_{\mathrm{w}}/M_{\mathrm{n}}{}^{b}$	conversion [c] %
1	bpy	toluene	2.4	8.4	1.5	25
2	bpy	acetonitrile	3.2	5.4	1.6	35
3	HMTETA	toluene	7.1	6.7	1.3	79
4	HMTETA	acetonitrile	3.9	5.8	1.5	43
5	PMTETA	toluene	3.2	4.6	1.6	34
6	PMTETA	acetonitrile	2.9	5.1	1.5	32
7	Me_6TREN	toluene	-	-	-	gelation
8	Me_6TREN	acetonitrile	-	-	-	gelation

[a] All runs are performed by solution polymerization ($[\mathrm{Monomer}]_0$: 1.0 M, for 96 h). $[\mathrm{Monomer}]_0/[\mathrm{Initiator}]_0/[\mathrm{CuBr}]_0/[\mathrm{Ligand}]_0$ = 50/1/1/1; $[\mathrm{Monomer}]_0/[\mathrm{Initiator}]_0/[\mathrm{CuBr}]_0/[\mathrm{bpy}]_0$ = 50/1/1/2. [b] Determined by SEC measurement in $CHCl_3$ relative to polystyrene. [c] Determined by ^{1}H-NMR spectroscopy; solvent $CDCl_3$.

Oxone Oxidation of Poly(ETEMA) to Poly(ESEMA). Oxone oxidation of poly(ETEMA) was performed in DMF at r.t. for 24 h to afford poly(ESEMA) (Scheme 2). Its ^{1}H-NMR spectrum is consistent with its expected structure. The extent of oxidation was estimated using the intensity ratio of the signals at 2.68–2.85 (OCH_2CH_2S) and 3.27–3.50 (m, $OCH_2C\mathit{H}_2SO_2$) ppm (Figure S3). The oxidation was also confirmed by IR spectrum, in which bands ascribed to S=O stretching was observed (Figure S3). The molecular weight (M_n=7.2×10^3) of after oxidation estimated by SEC measurement was similar to the parent poly(ETEMA) (M_n=6.7×10^3).

Preparation of a Stainless Steel Anode Coated with poly(ESEMA). Poly(ESEMA) (M_n=7.2×10^3 M_w/M_n=1.8) was stirred in DMF and DMF/BuOH (4 mL) for 15 min at 60˚C to obtain a homogeneous solution and the dispersions, respectively. For the deposition of poly(ESEMA) onto a stainless steel electrode by EPD, the distance between the stainless steel electrodes was 7.5 mm, and the deposition time was 90 s with a current of 1–2 mA. The results are summarized in Table 2. Although DMF (homogeneous) solution of poly(ESEMA) did not show any deposits on the stainless surface (run 1), a transparent film was formed on the 0.2 × 15 × 25 mm electrode from the DMF/BuOH dispersions [runs 2 and 3, and Figure 5(a)]. Conversely, the poly(ester-sulfone) film, reported by us previously was opaque [Figure 5(b)].[12c,d] It seems that the transparency of the poly(ESEMA) is a function of its methacrylate backbone. The structure of poly(ESEMA) after EPD was confirmed by ^{1}H-NMR (Figure 6) and FT-IR (Figure S3) spectroscopies. Comparison of the ^{1}H-NMR spectra of poly(ESEMA) before and after deposition onto the electrode (Figure 6) indicates that EPD did not change its structure.

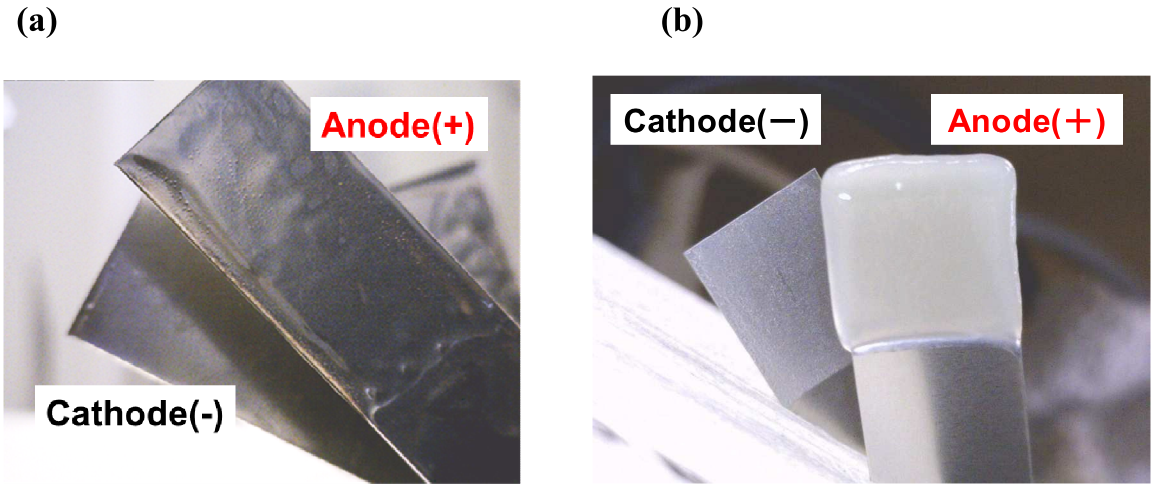


Figure 5. Photographs of the anode-selective electrophoretic deposition of (a) poly(ESEMA) (this work) onto a stainless steel electrode and (b) poly(ester-sulfone).[12d]

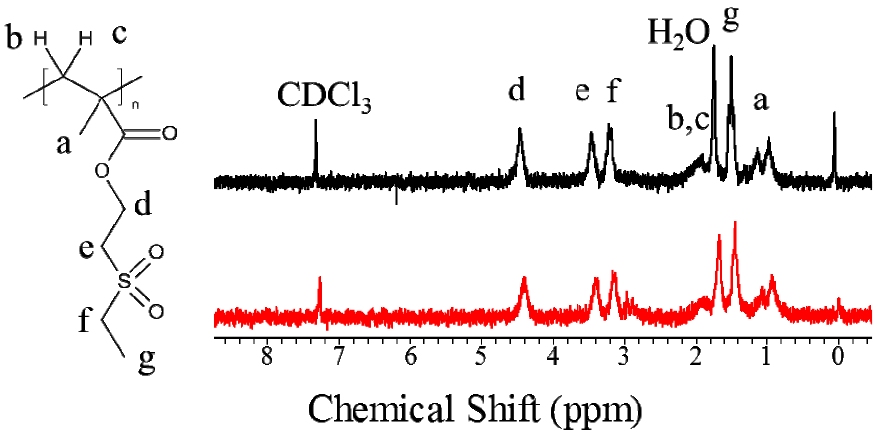


Figure 6. ^{1}H-NMR spectra poly(ESEMA) before (black) and after EPD (red).

Table 2. EPD Coating of Poly(ESEMA).[a]

run	solvent	zeta potential[b]	coating	
	DMF[a]:BuOH (v/v)	mV	electrode selectivity	state
1	1:0	–16.9	not deposited	not deposited
2	1:2	–35.4	anode	transparent
3	1:3	–46.5	anode	transparent

[a] M_n=7.2×10^3, M_w/M_n=1.8 in *N,N*-dimethylformamide (polymer concentration: 6 g/L).

[b] Determined by Zetasizer Nano ZS.

Zeta Potential Measurements of Poly(ESEMA) Dispersions

To characterize its electrophoretic behavior, the zeta potentials of poly(ESEMA) dispersions were measured in different ratios of BuOH and DMF (v/v). When the zeta potential value was between –46.5 and –35.4 mV (Table 2), the suspensions were stable and showed the anode-selective EPD behavior, indicating that the dispersion were surrounded by negative charge as shown in Figure 1. We expected that this is the reason for the anode selective deposition. Conversely, the zeta potential of poly(ETEMA) dispersion in DMF/BuOH (1/2, v/v) did not show remarkable negative value and did not move to the anode in the electrophoresis (please see Figure S4, right). Furthermore, as another control, dipping (not electrophoretic deposition but) of poly(ESEMA) dispersion was demonstrated under the same condition to confirm whether electrical current is essential or not for the deposition, in which the any electrophoretic deposition couldn't be confirmed onto both (anode and cathode) of stainless steel electrodes (please see Figure S4, left). The results for poly(ESEMA) are similar to our observation that our poly(ester-sulfone) prepared via thiol-ene click polymerization shows anode-selective deposition behavior.

Conclusions For this article, a sulfide-containing methacrylate was prepared by 2-(ethylthio)ethanol esterification of methacryloyl chloride. Copper-catalyzed ATRP of the sulfide-containing methacrylate was carried out and subsequently oxidized the polymer to synthesize the electrophoretic vinyl polymer containing pendent sulfones, poly(ESEMA). In our survey of ATRP conditions, control of the molecular weight of poly(ETEMA) was best when HMTETA served as the Cu(I) ligand and toluene as the solvent ($M_n = 6.7 \times 10^3$, $M_w/M_n = 1.3$). Poly(ESEMA) containing pendent sulfones via sulfone oxidation of poly(ETEMA) (oxidation, 90%) could be selectively coated onto a stainless-steel anode by EPD, in which the deposited film was trans parent. The selective EPD of poly(ESEMA) is similar to our recent finding that a sulfone-containing polyester shows anode-selective deposition behavior. These fundamental results should allow for widespread use of this EPD technique for smart coating of metals using ATRP strategies. The polyacrylates have extensibility, transparency, and flexibility and are primarily utilized in textile, paint, coating, adhesives. We are planning organic/inorganic hybrid containing bioactive glass or TiO_2 and expected applications for bone-regeneration and self-cleaning materials, respectively.

ASSOCIATE CONTENT

Supporting Information

^1H NMR spectra and results of control experiments for the EPD of produced polymethacrylates. This material is available free of charge via the Internet

REFERENCES

(1) J. Lyklema, *Fundamentals of Interface and Colloid Science* 1995, *2*, p. 3.208.

(2) R. J. Hunter, *Foundations of Colloid Science* 1989, Oxford University Press, New York, NY.

(3) S.S. Dukhin and B.V. Derjaguin, In: E Matievich. ed. *Elecirokinetic Phenomena. Surface and Colloid Science,. 7*, New York, Toronto: John Wiley and Sons. 1974, 2.

(4) W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal Dispersions* 1989, Cambridge University Press., Cambridge and New York

(5) H. R. Kruyt, *Colloid Science: Irreversible Systems*; H.R. Kruyt, Ed.; Elsevier: Amsterdam, 1952; Vol. 1, 16-17.

(6) A. S. Dukhin and P. J. Goetz, "Ultrasound for Characterizing Colloids. Particle Sizing, Zeta Potential, Rheology", New York, Elsevier, 2002.

(7) F. F. Reuss, *Mem. Soc. Imperiale Naturalistes de Moscow* 1809, *2*, 327.

(8) J. Sambrook, E. F. Fritsch and T. Maniatis, Molecular Cloning: A Laboratory Manual, 2nd Edition. Cold Spring Harbor Press NY 1989, pp18.47-18.59.

(9) (a) A. R. Boccaccini, S. Keim, R. Ma and L. I. Zhitmirsky, *J. R. Soc. Interface* 2010, *7*, 581-613. (b) J. Gastillo, M. Dimaki and W. E. Svendsen, *Integr. Biol.* 2009, *1*, 30–42. (c) S. W. Lee and A. M. Belcher, *Nano Lett.* 2004, *4*, 387-390. (d) L. Guo, *J. Adv. Mater.* 2007, *19*, 495–513.

(10) (a) P. Sarker and P. S. Nicholson, *J. Am. Ceram. Soc.* 1996, *79*, 1987-2002. (b) J. A. Roether, A. R. Boccaccini, L. L. Hench, V. Maquet, S. Gautier, and R. Jérôme, *Biomaterials*, 2002, *23*, 3871-3878. (c) I. Corni, N. Neumann, S. Novak, K. König, P.

Veronesi, Q. Chen, M. P. Ryan and A. R. Boccaccini, *Surf. Coat. Technol.* 2009, *203*, 1349-1359. (d) F. Pishbin, A. Simchi, M. P. Ryan and A. R. Boccaccini, *Surf. Coat. Technol.* 2011, *205*, 5260-5268. (e) H. H. Rodriguez, G. Vargas and D. A. Cortés, *Ceram. Int.* 2008, *34*, 1303-1130. (f) O. O. Van der Biest and L. J. Vandeperre, *Annu. Rev. Mater. Sci.* 1999, *29*, 327-352. (g) A. R. Boccaccini and I. Zhitomirsky, *Curr. Opin. Solid State Mater. Sci.* 2002, *6*, 251-260. (h) R. Ma and I. Zhitomirsky, *J. Alloy Compd*. 2011, *509*, S510-S513. (i) Y. Wang, I. Deen and I. Zhitomirsky, *J. Colloid Interface Sci.* 2011, *362*, 367-374. (j) A. R. Boccaccini, C. Peters, J. A. Roether, D. Eifler, S. K. Misra and E. J. Minay, *J. Mater. Sci*. 2006, *41*, 8152-8159. (k) X. F. Xiao and R. F. Liu, *Mater. Lett*. 2006, *60*, 2627-2632.

(11) (a) A. Takasu, Y. Oishi, Y. Iio, Y. Inai and T. Hirabayashi, *Macromolecules* 2003, *36*, 1772-1774. (b) A. Takasu, Y. Iio, Y. Oishi, Y. Narukawa and T. Hirabayashi, *Macromolecules* 2005, *38*, 1048-1050. (c) A. Takasu, Y. Iio, T. Mimura and T. Hirabayashi, *Polym. J.* 2005, *37*, 946-953. (d) in water: A. Takasu, A. Takemoto and T. Hirabayashi, *Biomacromolecules* 2006, *7*, 6–9. (e) PLA: A. Takasu, Y. Narukawa and T. Hirabayashi, *J. Polym. Sci.; Part A: Polym. Chem.* 2006, 44, 5247–5253. (f) combination with ROP: A. Takasu, H. Tsuruta, Y. Narukawa, Y. Shibata, M. Oshimura and T. Hirabayashi, *Macromolecules.* 2008, *41*, 4688-4693. (g) customized

catalyst: A. Takasu, T. Makino and S. Yamada, *Macromolecules.* 2010, *43*, 144-149. (h) microwave-assisted: S. Yamada and A. Takasu, *Polym. J.* 2011, *43*, 1003-1007. (i) hydroxyl: A. Takasu, Y. Shibata, Y. Narukawa and T. Hirabayashi, *Macromolecules* 2007, *40*, 151–153. (j) hydroxyl: Y. Shibata and A. Takasu, *J. Polym. Sci.; Part A: Polym. Chem.* 2009, *47*, 5747-5759. (k) mercapto: K. Yamamoto and A. Takasu, *Macromolecules* 2010, *43*, 8519-8523. (l) disulfide: Y. Sato and A. Takasu, *Polym. J.* 2010, *42*, 956-959.

(12) (a) Y. Nagao and A. Takasu, *Macromol. Rapid Commun.* 2009, *30*, 199-203. (b) Y. Nagao and A. Takasu, *J. Polym. Sci.; Part A: Polym. Chem.* 2011, *48*, 4207–4218. (c) Y. Nagao, A. Takasu and A. R. Boccaccini, *Macromolecules*, 2012, *45* , 3326–3334. (d) T. Fukuoka and, A. Takasu, *RSC Advances*, 2014, *4*, 15983-15994.

(13) As a preliminary result: As a preliminary result: T. Kameyama, and A. Takasu, *Polym. Prepr. (Am. Chem. Soc. Div. Polym.)* 2014, POLY-398.

(14) J. Lin, A. Tarel, Y. Yusuf and I. Hatsuo, *Macromolecules*, 2011, *44*, 767-772.

(15) F. De´ne`s, C. H. Schiesserb and P. Renaud, *Chem. Soc. Rev.*, 2013, *42*, 7900-7942.

(16) Y. Zheng, K. J. Thurecht and W. Wang, *J. Polym. Sci.; Part A: Polym. Chem.* 2012, 50, 629–637.

For Table of Contents Use Only

Graphical Abstract for Polymer Chemistry

	A Vinyl Polymer Having Pendent Sulfones Prepared by Atom-Transfer Radical Polymerization of Sulfide-Containing Methacrylate and Electrophoretic Transparent Coating on Stainless-Steel Anode *Tomomi Kameyama and Akinori Takasu**