

phorylcholine. In particular, the phosphorus concentration of the  $C_8F_{17}PC/LDPE$  film was significantly higher than that of other composite films with low molar  $C_8F_{17}PC$  ( $1.37 \times 10^{-5}$  mol, 1.7% w/w).

The  $15^\circ$  takeoff angle data indicate the composition of the outermost  $\sim 10$  Å of the samples; the  $75^\circ$  takeoff angle spectra assess the outer  $\sim 40$  Å.<sup>34</sup> Comparison of the atomic concentration obtained from XPS to the chemical composition of  $C_8F_{17}PC$  (C, 29.63%; O, 10.17%, N, 2.23; P, 4.92%; F, 51.33%) indicates that there is  $\sim 95\%$   $C_8F_{17}PC$  in the outer 10 Å and  $\sim 75\%$   $C_8F_{17}PC$  in the outer 40 Å when the compositions are calculated from the concentration of fluorine. From the concentration of phosphorus, there is  $\sim 55\%$   $C_8F_{17}PC$  in the outer 10 Å and  $\sim 40\%$   $C_8F_{17}PC$  in the outer 40 Å. The molecular size of  $C_8F_{17}PC$  is  $\sim 18$  Å, and the fluoroalkyl chains of  $C_8F_{17}PC$  were partially oriented to the outer surface. When  $C_6F_{13}PC$  and  $C_{10}F_{21}PC$  were added to LDPE with a similar concentration ( $2.74 \times 10^{-5}$  mol), the surface coverage calculated from the concentration of fluorine was  $\sim 55\%$  and  $\sim 60\%$  in the outer 10 Å, respectively. For  $C_6F_{13}PC$ , the surface coverage calculated from the concentration of phosphorus was 30%; the XPS elemental concentrations at  $15^\circ$  and  $75^\circ$  were quite similar. This result indicated that the distribution of  $C_6F_{13}PC$  in the outer 40 Å was uniform. Moreover, the concentration of fluorine in the outer 40 Å was higher than that in the outer 10 Å when  $C_{10}F_{21}PC$  ( $2.74 \times 10^{-5}$  mol) was added. The surface activity and dispersity of  $C_8F_{17}PC$  in the LDPE matrix may be optimum for the enrichment of LDPE film surfaces.

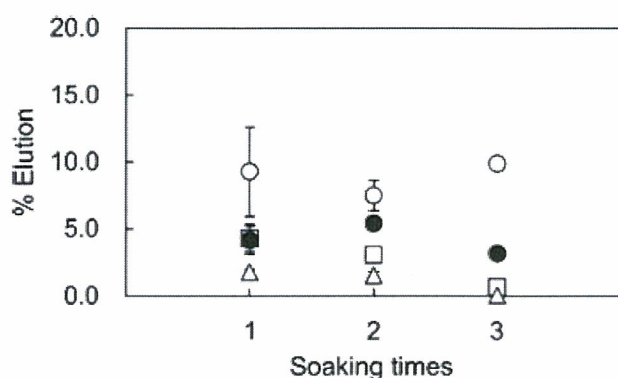
Surface contact angle data for polymer films were measured with water, as shown in Table II. The water contact angle data for the LDPE film was  $\theta_A/\theta_R = 97^\circ/81^\circ$ . The contact angles decreased with an increase in the composition of the PC additives. On the  $C_{16}PC/LDPE$  surface, the contact angles reached  $\theta_A/\theta_R = 43^\circ/15^\circ$  when the composition of  $C_{16}PC$  was  $6.86 \times 10^{-5}$  mol (5.3% w/w). At this concentration, the surface coverage of  $C_{16}PC$  was  $\sim 15\%$  calculated from XPS data and was lower than that of fluoroalkylated PCs. The water contact angles of the  $C_{16}PC/LDPE$  film were then relatively high.

The surface contact angles ( $\theta_A/\theta_R$ ) of  $C_8F_{17}PC/LDPE$  were dramatically decreased at  $28^\circ/8^\circ$  with  $2.74 \times 10^{-5}$  mol  $C_8F_{17}PC$  (3.3% w/w) and  $17^\circ/<5^\circ$  with  $6.86 \times 10^{-5}$  mol  $C_8F_{17}PC$  (7.9% w/w). The effects of  $C_6F_{13}PC$  and  $C_{10}F_{21}PC$  on improving surface wettability were less than that of  $C_8F_{17}PC$  because of their low surface coverage.

Figure 4 shows % elution of PC additives from composite films after soaking films containing  $6.86 \times 10^{-5}$  mol of PC additives in ethanol for 2 h. The elution amount of fluoroalkyl PCs was significantly lower than that of alkyl PCs. In particular, the elution amount of  $C_8F_{17}PC$  and  $C_{10}F_{21}PC$  was reduced with an increase in the soaking frequency and elution did not occur after three soakings. The elution amount of PC additives from LDPE films in water was also determined to be much lower than that in ethanol and  $C_8F_{17}PC$  after 24 h of soaking under gentle shaking. The amount was 0.4% or less for  $6.86 \times 10^{-5}$  mol (7.9% w/w) and 0.1% or less for  $1.37 \times 10^{-5}$  mol

TABLE II  
Water Contact Angle Data for Polymer Films

Films	Composition of PC additives		$\theta_A/\theta_R$ ( $^\circ$ )	
	(mol)	(% w/w)	Post-preparation	After soaking in EtOH
PE			98/81	105/92
$C_{16}PC/PE$	$6.86 \times 10^{-6}$	0.6	87/61	
	$1.37 \times 10^{-5}$	1.1	87/68	
	$2.74 \times 10^{-5}$	2.2	64/30	75/17
	$6.86 \times 10^{-5}$	5.3	43/15	41/17
$C_{10}F_{21}PC/PE$	$6.86 \times 10^{-6}$	1.0	86/65	
	$1.37 \times 10^{-5}$	2.0	93/55	
	$2.74 \times 10^{-5}$	3.8	90/59	81/26
	$6.86 \times 10^{-5}$	9.1	38/10	91/21
$C_8F_{17}PC/PE$	$6.86 \times 10^{-6}$	0.9	82/67	
	$1.37 \times 10^{-5}$	1.7	81/8	
	$2.74 \times 10^{-5}$	3.3	28/8	16/10
	$6.86 \times 10^{-5}$	7.9	17/<5	18/10
$C_6F_{15}PC/PE$	$6.86 \times 10^{-6}$	0.7	84/62	
	$1.37 \times 10^{-5}$	1.4	79/29	
	$2.74 \times 10^{-5}$	2.8	68/32	94/55
	$6.86 \times 10^{-5}$	6.8	26/11	26/10



**Figure 4** Percentage elution of PC additives from composite films soaked in ethanol. Filled circle: C<sub>16</sub>PC/PE, Open circle: C<sub>6</sub>F<sub>13</sub>PC/PE, Open square: C<sub>8</sub>F<sub>17</sub>PC/PE, Open triangle: C<sub>10</sub>F<sub>21</sub>PC/PE.

(1.7% w/w). This solvent dependence of the elution might be due to the solubility of the PC additives.

Molecular design such as macromolecular approaches to improve stability and further surface treatments to reduce elution of PC additives from composite films are now under study.

Figure 5 shows photographs of typical water drops on LDPE and C<sub>8</sub>F<sub>17</sub>PC/LDPE after the elution test in ethanol. When a water drop on LDPE film is round in shape, the shape spreads out completely on the C<sub>8</sub>F<sub>17</sub>PC/PE film with  $2.74 \times 10^{-5}$  mol of C<sub>8</sub>F<sub>17</sub>PC (3.3% w/w). The surface wettability of the composite film was present even after ethanol soaking, as shown in Table II.

#### Mechanical properties of LDPE films containing PC additives

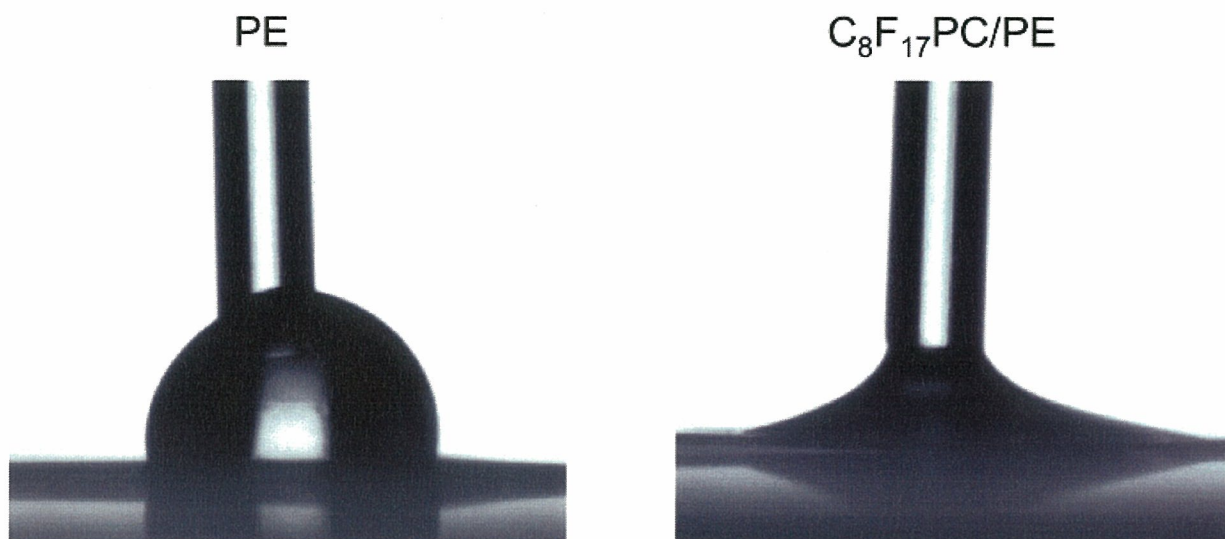
Table III shows the mechanical properties of the composite films. By mixing PC additives, Young's modu-

lus of films was relatively higher than that of the LDPE film. Every PC additive was a powdery solid at the measuring temperature and the composite films were then rigid. When the fracture strength was not changed by the addition of PC additives, the elongation of the composite films was reduced. This phenomenon might be due to an incompatibility of the PC additives and LDPE matrix. Although C<sub>16</sub>PC has a long alkyl chain, which would be more compatible with PE compared with that of the perfluoroalkylated chain, the elongation of the composite film with C<sub>16</sub>PC was much less. Fluoroalkylated PCs effectively enriched the LDPE surface and had less influence on the bulk property of the LDPE films.

#### CONCLUSIONS

Perfluoroalkylated PCs are potential additives for improving the wettability of LDPE film. Perfluoroalkylated PC was spontaneously enriched on the film surface using a heat-press technique. High wettability can be obtained without chemical or physical treatment. In addition, no solvent was needed. In particular, C<sub>8</sub>F<sub>17</sub>PC, which has an octafluoromethylene chain, is most effective for achieving this. The thermal stability of phosphorylcholine groups has been assured at 150°C.<sup>35</sup> Therefore, perfluoroalkylated PCs can be applied for surface modification of other thermoplastic polymers.

There has been a considerable amount of physicochemical- and biotechnological-related interest in PC-enriched surfaces, which show unique properties such as hydrophilicity,<sup>36</sup> zero  $\zeta$ -potential (neutral),<sup>37</sup> high lubrication,<sup>38</sup> and biocompatibility.<sup>39</sup> Therefore, surface modification with spontaneous PC enrichment is important for producing high performance polymeric materials.



**Figure 5** Photographs of water drops on PE and C<sub>8</sub>F<sub>17</sub>PC/PE films (C<sub>8</sub>F<sub>17</sub>PC =  $1.37 \times 10^{-5}$  mol) after elution test.

TABLE III  
Mechanical Properties of Polymer Films

	Composition of PC additives		Young's modulus (MPa)	Fracture strength (MPa)	Averaged fracture strain (%)
	(mol)	(% w/w)			
PE			61.9 ± 1.5	5.83 ± 0.32	80.1
C <sub>16</sub> PC/PE	2.74	2.2	71.6 ± 4.4	5.49 ± 0.44	45.9
	6.86	5.3	60.8 ± 2.7	5.45 ± 0.32	46.3
C <sub>10</sub> F <sub>21</sub> /PC/PE	2.74	3.8	75.7 ± 5.3	5.72 ± 0.36	52.1
	6.86	9.1	68.3 ± 3.1	5.49 ± 0.25	58.3
C <sub>8</sub> F <sub>17</sub> /PC/PE	2.74	3.3	79.3 ± 6.9	6.00 ± 0.23	57.4
	6.86	7.9	68.9 ± 3.6	5.53 ± 0.19	56.5
C <sub>6</sub> F <sub>15</sub> /PC/PE	2.74	2.8	75.2 ± 1.1	5.68 ± 0.43	60.3
	6.86	6.8	68.5 ± 4.4	5.56 ± 0.28	54.1

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# Surface modification with well-defined biocompatible triblock copolymers Improvement of biointerfacial phenomena on a poly(dimethylsiloxane) surface

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## Abstract

To improve interfacial phenomena of poly(dimethylsiloxane) (PDMS) as biomaterials, well-defined triblock copolymers were prepared as coating materials by reversible addition-fragmentation chain transfer (RAFT) controlled polymerization. Hydroxy-terminated poly(vinylmethylsiloxane-co-dimethylsiloxane) (HO-PV<sub>i</sub>D<sub>m</sub>MS-OH) was synthesized by ring-opening polymerization. The copolymerization ratio of vinylmethylsiloxane to dimethylsiloxane was 1/9. The molecular weight of HO-PV<sub>i</sub>D<sub>m</sub>MS-OH ranged from  $(1.43 \text{ to } 4.44) \times 10^4$ , and their molecular weight distribution ( $M_w/M_n$ ) as determined by size-exclusion chromatography equipped with multiangle laser light scattering (SEC-MALS) was 1.16. 4-Cyanopentanoic acid dithiobenzoate was reacted with HO-PV<sub>i</sub>D<sub>m</sub>MS-OH to obtain macromolecular chain transfer agents (macro-CTA). 2-Methacryloyloxyethyl phosphorylcholine (MPC) was polymerized with macro-CTAs. The gel-permeation chromatography (GPC) chart of synthesized polymers was a single peak and  $M_w/M_n$  was relatively narrow (1.3–1.6). Then the poly(MPC) (PMPC)-PV<sub>i</sub>D<sub>m</sub>MS-PMPC triblock copolymers were synthesized. The molecular weight of PMPC in a triblock copolymer was easily controllable by changing the polymerization time or the composition of the macro-CTA to a monomer in the feed. The synthesized block copolymers were slightly soluble in water and extremely soluble in ethanol and 2-propanol.

Surface modification was performed *via* hydrosilylation. The block copolymer was coated on the PDMS film whose surface was pretreated with poly(hydromethylsiloxane). The surface wettability and lubrication of the PDMS film were effectively improved by immobilization with the block copolymers. In addition, the number of adherent platelets from human platelet-rich plasma (PRP) was dramatically reduced by surface modification. Particularly, the triblock copolymer having a high composition ratio of MPC units to silicone units was effective in improving the surface properties of PDMS.

By selective decomposition of the Si-H bond at the surface of the PDMS substrate by irradiation with UV light, the coating region of the triblock copolymer was easily controlled, resulting in the fabrication of micropatterns. On the surface, albumin adsorption was well manipulated.

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**Keywords:** Phosphorylcholine polymer; PDMS; RAFT polymerization; Block copolymer; Surface modification; Non-fouling; Lubrication

## 1. Introduction

Poly(dimethylsiloxane) (PDMS) is one of the most valuable polymers for use in biomedical devices such as catheters, tracheoesophageal voice prostheses, finger joints, percutaneous devices, dentures, etc. [1]. One of the more recent trends in PDMS applications is microfluidic devices for biosensors or

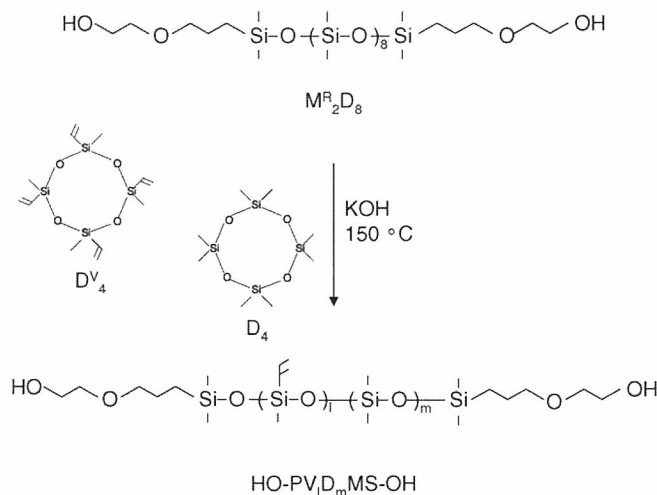
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biochips [2–5]. PDMS has flexibility, high gas permeability, processability, flexible surface chemistry, and optical transparency. However, the interface of the PDMS surface with the biological environment is inadequate, and non-specific biofouling, i.e., protein adsorption and cell adhesion frequently occurs on the surface [6–9]. Biofouling induces contamination, inflammation, infection, and the reduction of material function. High friction of PDMS surface is also unfavorable nature for medical applications. These disadvantages of PDMS are due to hydrophobicity of the surface, necessitating surface modification. The formation of a hydrophilic surface on PDMS by using oxidation [10,11] and hydrophilic polymers [12–14] is proposed as a method of solving interfacial problems. Poly(ethylene glycol) (PEG) is one of the principal polymer candidates for reducing non-specific fouling at the biointerface [15]. For PDMS, covalent bonding onto PDMS surfaces of PEG-functionalized silanes [16–18] or amine-functionalized silanes to further react with PEG-moieties [19,20] has generally been employed. PEGylation is very effective in reducing biofouling. However, cell adhesion was observed on surfaces after long-term exposure in a culture medium [21].

To obtain other types of reliable non-fouling surfaces, we have been studying 2-methacryloyloxyethyl phosphorylcholine (MPC) polymers synthesized as biomimetics in biomembrane structures [22–24]. There have been some reports describing the surface modification of PDMS with MPC. Plasma-induced graft polymerization was applied as a primary process [25,26]. However, this modification has limitations in increasing the surface composition of MPC units because the phosphorus concentration remained low compared with the theoretical amount calculated from the chemical structure of MPC. Goda et al. recently reported the photo-induced grafting of MPC on a PDMS surface [14]. They succeeded in improving the composition of the MPC units on the PDMS surface compared with plasma polymerization. Moreover, the surface friction of PDMS surface effectively reduced by the surface modification. Although surface modification with MPC polymers *via* the grafting process is valuable for achieving a non-fouling surface on PDMS, their use precludes accurate control of the polymer structure and specific equipment is required.

Surface-coating processes are more applicable as methods of surface modification. Generally, organic solvent is used for the surface modification of PDMS, and the coating of hydrophilic polymer on PDMS is difficult because the surface is hydrophobic and has a low surface energy. The surface modification of PDMS using polar solvent is still limited [27]. A precise molecular design of an MPC polymer having the desired solubility and anchors that have an affinity to the PDMS surface is needed for reliable surface modification.

To produce well-defined polymers, controlled “living” radical polymerization has been explored [28]. Atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization are very useful for achieving this process because they can be applied to a wide variety of monomers [29–35]. We have prepared poly(MPC) (PMPC) brush on a silicon wafer *via* ATRP and clarified that plasma protein adsorption and cell adhesion were effectively reduced



Scheme 1. Synthetic route of hydroxy-terminated poly(vinylmethylsiloxane-co-dimethylsiloxane) (OH-PV<sub>I</sub>D<sub>m</sub>MS-OH).

on the surface with a polymer brush thickness of only 5 nm [36]. While the use of well-defined polymer brush with ATRP is considerable theoretical and experimental interests in control of surface properties, some specific conditions for the reaction are needed and still difficult to use as a common method of surface modification.

This paper primary reports surface modification of PDMS with well-defined ABA-type triblock copolymers composed of poly(MPC) (PMPC) blocks (A) and central silicone blocks (B) with anchoring vinyl groups by using a simple coating process. We also determine the effects of structures of the copolymers on the surface properties and clarify that the block copolymers have great power to improve interfacial phenomena of PDMS as biomaterials.

## 2. Materials and methods

### 2.1. Materials

Dicyclohexylcarbodiimide (DCC) and 4-dimethylamino-pyridine was purchased from Kanto Chemical Co. Ltd., Japan and used without further purification. 4-Cyanopentanoic acid dithiobenzoate was synthesized according to the method reported by McCormick and co-workers [34]. Octamethylcyclotetrasiloxane (D<sub>4</sub>), tetramethyl tetra vinyl cyclotetrasiloxane (D<sub>4</sub><sup>V</sup>), and hydroxyethoxypropyl dimethylsilyl-terminated oligo(dimethylsiloxane) (M<sub>2</sub><sup>R</sup>D<sub>8</sub>, n = 8) were kindly provided by Shin-Etsu Chemical Co. Ltd. MPC was synthesized by the method previously described and purified by recrystallization from acetonitrile [23].

Hydroxy-terminated poly(vinylmethylsiloxane-co-dimethylsiloxane)s (HO-PV<sub>I</sub>D<sub>m</sub>MS-OH) were synthesized by conventional ring-opening polymerization of cyclosiloxane compounds using KOH (20 ppm) as a catalyst (Scheme 1). The molecular weight of hydroxy-terminated silicones was controlled by changing the ratio of D and M<sub>2</sub><sup>R</sup>D<sub>8</sub>. The ratio of D<sub>4</sub><sup>V</sup> and D<sub>4</sub> was adjusted at 1/9 in every case. The synthetic condition is summarized in Table 1. The absolute molecular weight (M<sub>w</sub>)

Table 1  
Synthetic results of hydroxy-terminated poly(dimethylsiloxane-co-vinylmethylsiloxane) (OH-PV<sub>l</sub>D<sub>m</sub>MS-OH)

Code	M <sub>2</sub> <sup>R</sup> D <sub>8</sub> /(Me <sub>2</sub> SiO) <sub>4</sub> /(MeViSiO) <sub>4</sub> (mol)	Me <sub>2</sub> SiO/MeViSiO (molar fraction)		M <sub>w</sub> (×10 <sup>4</sup> )	M <sub>w</sub> /M <sub>n</sub>
		In feed	In copolymer <sup>a</sup>		
OH-PV <sub>17</sub> D <sub>173</sub> MS-OH	1/37/5	0.89/0.11	0.91/0.09	1.43 <sup>b</sup>	1.16 <sup>b</sup>
OH-PV <sub>32</sub> D <sub>324</sub> MS-OH	1/82/10	0.89/0.11	0.91/0.09	2.68 <sup>b</sup>	1.16 <sup>b</sup>
OH-PV <sub>53</sub> D <sub>537</sub> MS-OH	1/172/20	0.90/0.10	0.91/0.09	4.44 <sup>c</sup>	–

<sup>a</sup> Determined by <sup>1</sup>H NMR.

<sup>b</sup> Absolute molecular weight: determined by MALLS.

<sup>c</sup> Calculated from apparent molecular weight.

of the HO-PV<sub>l</sub>D<sub>m</sub>MS-OH was determined by size-exclusion chromatography equipped with multiangle laser light scattering (SEC-MALS) analysis with a Shodex KF-806L column and a Wyatt Dawn HELEOS detector. The apparent molecular weights of the HO-PV<sub>l</sub>D<sub>m</sub>MS-OH were also measured using gel-permeation chromatography (GPC) through a Shodex KF-803 column using a calibration curve based on linear polystyrene standards. THF was used as the GPC solvent.

To obtain a macromolecular chain transfer agent (macro-CTA), DCC (4.0 molar to HO-PV<sub>l</sub>D<sub>m</sub>MS-OH) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was added dropwise to a CH<sub>2</sub>Cl<sub>2</sub> (100 mL) solution of 4-cyanopentanoic acid dithiobenzoate (2.4 molar to HO-PV<sub>l</sub>D<sub>m</sub>MS-OH) and HO-PV<sub>l</sub>D<sub>m</sub>MS-OH (30 g) and stirred for 20 h at 40 °C (Scheme 2). The solution was then filtered to remove any insoluble substances. After evaporation of CH<sub>2</sub>Cl<sub>2</sub>, the reaction mixture was washed with methanol until the methanol was colorless, diluted with chloroform, washed three times with brine, dried over MgSO<sub>4</sub>, and concentrated. A viscous liquid was obtained. The chemical structure of macro-CTA was confirmed by <sup>1</sup>H NMR (α-500, JEOL, Tokyo, Japan) and FT-IR spectroscopy (FT-500, Jasco, Tokyo, Japan). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = macro-CTA: -0.2 to 0.2 (m; Si-CH<sub>3</sub>), 1.9 (s; CN-C-CH<sub>3</sub>), 2.35–2.75 (m; -C-CH<sub>2</sub>-CH<sub>2</sub>-COOH), 5.6–5.8 (m; -CH=CH<sub>2</sub>), 5.8–6.0 (m; -CH=CH<sub>2</sub>), 7.3–7.9 (m; Ph).

## 2.2. Synthesis of block copolymers

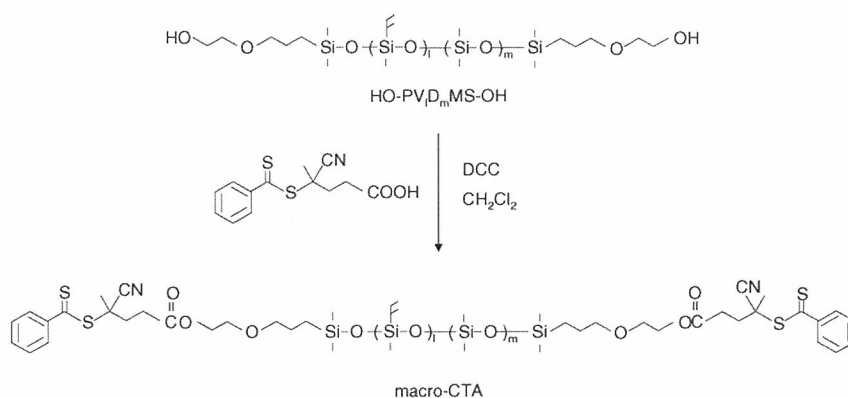
Because the radical for polymerization was sensitive to air, all reactions were performed in an argon gas atmo-

sphere. The synthetic condition of the block copolymers is summarized in Table 2. Typically, α,α'-azobisisobutyronitrile (AIBN, 0.025 mmol) was introduced through a polymerization tube. MPC (4.43 g, 15.0 mmol) and macro-CTA (PD<sub>324</sub>V<sub>32</sub>MS, 0.05 mmol) were desorbed in a toluene/ethanol (1/1) mixture, and the volume of the solution was adjusted to 30 mL. Then, argon gas was passed through the solution for 30 min to eliminate oxygen. The solution was heated at 70 °C and stored with gentle shaking for given periods. After polymerization, the block copolymer was precipitated into THF, then dissolved in ethanol, and again precipitated into THF. The precipitation was dried *in vacuo*. The synthetic route of the PMPC-PV<sub>l</sub>D<sub>m</sub>MS-PMPC triblock copolymers is shown in Scheme 3.

The number- and weight-averaged molecular weights of the block copolymers were measured with a Tosoh GPC system with a refractive index detector and size-exclusion columns, Shodex, SB-804 HQ and SB-806M HQ with a poly(ethylene glycol) (PEG, Tosoh standard sample) standard in 20 vol.% methanol containing 10 mM LiBr. The molar fraction of the MPC unit of block copolymer was also determined by phosphorus analysis.

## 2.3. Preparation of silicone substrate and surface functionalization

Silpot 184 PDMS prepolymer was mixed thoroughly with its cross-linking catalyst (10:1, w/w) and poured into a Petri dish. After the bubbles were removed from the prepolymer under reduced pressure, the films were cured at 100 °C for 3 h. The cured film was removed from the plate and cut into 1.4 cm diameter disks. The film disks were washed thoroughly with hexane



Scheme 2. Synthetic route of macro chain transfer agent (macro-CTA).

Table 2  
Synthetic results of PMPC–PV<sub>l</sub>D<sub>m</sub>MS–PMPC triblock copolymers

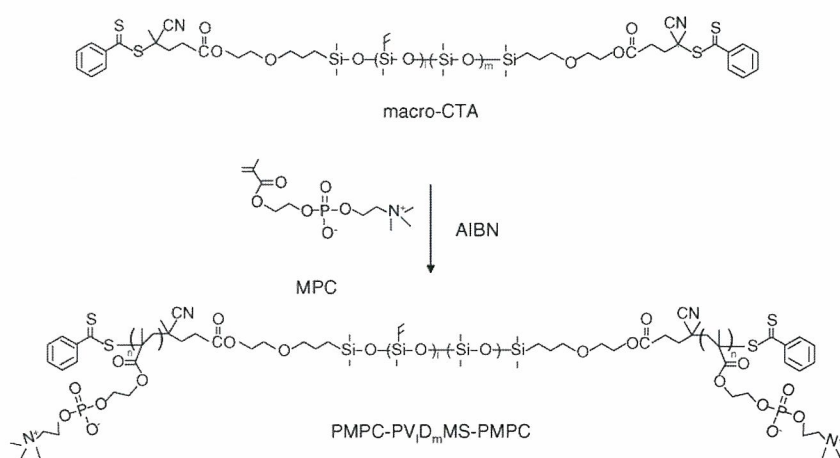
Code	Copolymers	MPC/macro-CTA/AIBN (mol) in feed <sup>a</sup>	PMPC <sub>PD(</sub> one side) in copolymer <sup>b</sup>	M <sub>w</sub> (×10 <sup>4</sup> ) <sup>c</sup>	M <sub>w</sub> /M <sub>n</sub>	PMPC/ silicone <sup>d</sup>
26–173	PMPC <sub>26</sub> –PV <sub>17</sub> D <sub>173</sub> MS–PMPC <sub>26</sub>	1.5 × 10 <sup>-2</sup> /1 × 10 <sup>-4</sup> /5 × 10 <sup>-5</sup>	26.0	2.32	1.27	0.27
35–173	PMPC <sub>35</sub> –PV <sub>17</sub> D <sub>173</sub> MS–PMPC <sub>35</sub>	1.5 × 10 <sup>-2</sup> /5 × 10 <sup>-5</sup> /2.5 × 10 <sup>-5</sup>	34.7	3.53	1.31	0.37
53–173	PMPC <sub>53</sub> –PV <sub>17</sub> D <sub>173</sub> MS–PMPC <sub>53</sub>	1.5 × 10 <sup>-2</sup> /2.5 × 10 <sup>-5</sup> /1.25 × 10 <sup>-5</sup>	52.7	6.85	1.41	0.55
54–324	PMPC <sub>54</sub> –PV <sub>32</sub> D <sub>324</sub> MS–PMPC <sub>54</sub>	1.5 × 10 <sup>-2</sup> /1 × 10 <sup>-4</sup> /5 × 10 <sup>-5</sup>	54.2	3.93	1.28	0.30
66–324	PMPC <sub>66</sub> –PV <sub>32</sub> D <sub>324</sub> MS–PMPC <sub>66</sub>	1.5 × 10 <sup>-2</sup> /5 × 10 <sup>-5</sup> /2.5 × 10 <sup>-5</sup>	66.3	6.23	1.41	0.37
119–324	PMPC <sub>119</sub> –PV <sub>32</sub> D <sub>324</sub> MS–PMPC <sub>119</sub>	1.5 × 10 <sup>-2</sup> /2.5 × 10 <sup>-5</sup> /1.25 × 10 <sup>-5</sup>	118.6	9.85	1.63	0.66
75–325	PMPC <sub>75</sub> –PV <sub>53</sub> D <sub>537</sub> MS–PMPC <sub>75</sub>	1.5 × 10 <sup>-2</sup> /1 × 10 <sup>-4</sup> /5 × 10 <sup>-5</sup>	75.3	8.47	1.47	0.26
99–537	PMPC <sub>99</sub> –PV <sub>53</sub> D <sub>537</sub> MS–PMPC <sub>99</sub>	1.5 × 10 <sup>-2</sup> /5 × 10 <sup>-5</sup> /2.5 × 10 <sup>-5</sup>	99.2	11.30	1.55	0.34
153–537	PMPC <sub>153</sub> –PV <sub>53</sub> D <sub>537</sub> MS–PMPC <sub>153</sub>	1.5 × 10 <sup>-2</sup> /2.5 × 10 <sup>-5</sup> /1.25 × 10 <sup>-5</sup>	152.2	16.64	1.63	0.52

<sup>a</sup> [MPC] = 0.5 mol/L; [CTA]/[AIBN] = 2; polymerization temperature 70 °C; solvent: ethanol/toluene = 1/1 (v/v).

<sup>b</sup> Determined by phosphorus analysis, PD: polymerization degree.

<sup>c</sup> Determined by GPC, eluent: MeOH/H<sub>2</sub>O = 20/80 with 10 mM LiBr.

<sup>d</sup> n × 2/(l + m), PMPC<sub>n</sub>–PV<sub>l</sub>D<sub>m</sub>MS–PMPC<sub>n</sub>.



Scheme 3. Synthetic route of PMPC–PV<sub>l</sub>D<sub>m</sub>MS–PMPC triblock copolymer.

and acetone and dried under *in vacuo* for 1 day at room temperature. The surface functionalization of the PDMS films was processed as previously described [37]. Briefly, the silicone films were incubated in a solution of poly(hydromethylsiloxane) (KF-99-P®):2-propanol (3:5, v/v) containing triflic acid as a catalyst (0.02 mL) with stirring for 15 min at room temperature. The silicone films were then removed from the solution and washed thoroughly with 2-propanol and hexane, then dried *in vacuo* for 1 day at room temperature. The presence of surface Si–H groups (absorption peak at 2167 cm<sup>-1</sup>) was confirmed by ATR-FT-IR.

#### 2.4. Surface modification of silicone films with PMPC–PV<sub>l</sub>D<sub>m</sub>MS–PMPC triblock copolymer

A solution (5 g) of 1 wt% PMPC–PV<sub>l</sub>D<sub>m</sub>MS–PMPC triblock copolymers desorbed in ethanol was prepared and Pt-catalyst (platinum–divinyltetramethylsiloxane complex) (two drops) was added to the polymer solution. The solution was dropped onto a Si–H functionalized silicone film and spin-coated at 4000 rpm for 10 s. The film was heated at 80 °C for 2 h, then rinsed by soaking in ethanol for 24 h at 50 °C. The ethanol was changed several times. The film was then dried *in vacuo*. Fig. 1 is

a schematic representation of the surface modification of PDMS with PMPC–PV<sub>l</sub>D<sub>m</sub>MS–PMPC triblock copolymers.

#### 2.5. Surface analysis

X-ray photoelectron spectroscopy (XPS) was performed on a Scienta ESCA-200 spectrometer with Al K $\alpha$ . Survey scans

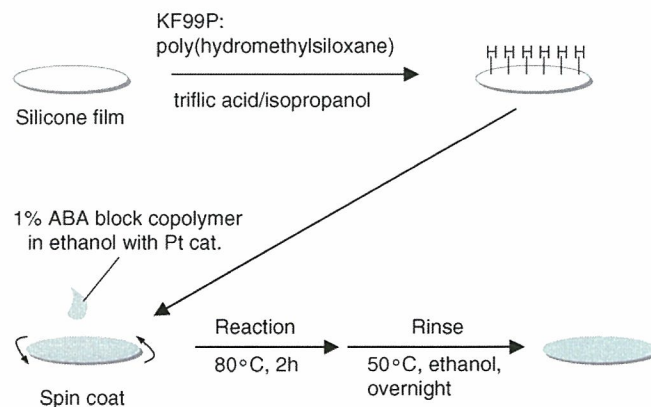


Fig. 1. Schematic representation of surface modification of PDMS with PMPC–PV<sub>l</sub>D<sub>m</sub>MS–PMPC triblock copolymer.

spectra of C 1s, O 1s, N 1s, and P 2p were obtained. All XPS data were collected at take off angles of  $75^\circ$  (between the specimen surface and the detector).

The dynamic contact angles for the samples were recorded as the probe fluid, water (deionized to  $18.2\text{ M}\Omega$ ), using a First Ten Angstroms FT-125 goniometer and Gilmont syringes. The advancing ( $\theta_A$ ) and receding ( $\theta_R$ ) contact angles were measured with addition to and withdrawal from the drop, respectively.

The surface frictional coefficients during startup and under steady state conditions were measured using a surface property tester (Heidon Type32, Shinto Science Co., Tokyo, Japan). Sample films ( $\phi = 1.4\text{ cm}$ ) were thoroughly wet with water before and during the measurements. The measurements were conducted by sliding the membrane under a 100 g load using a stainless steel ball (10 mm in diameter). The scan speed and scale were 10 mm/s.

### 2.6. Platelet adhesion test

Human platelet-rich plasma (PRP) was prepared from citrated whole blood by centrifugation. Polymer samples were placed in a 24-well tissue culture plate and secured with a silicone rubber ring. The PBS was allowed to stand in the wells overnight to equilibrate the surface. PRP was poured into each well and stored at room temperature for 60 min. The polymer surfaces in contact with PRP were observed by a scanning electron microscope (S-3400NX, Hitachi High-Technologies Co., Tokyo, Japan). The density of adherent platelets was determined by measuring lactic acid dehydrogenase (LDH) from the platelets [38]. After the PRP was incubated on the polymer samples, the samples were rinsed three times with PBS. The samples were then transferred to a new 24-well tissue culture plate. Triton X-100 (0.5 wt%, 1 mL) was introduced into each well and incubated for 30 min. The Triton X-100 solution (250  $\mu\text{L}$ ) was collected and the concentration of LDH from the adherent platelets was measured by the LDH-Cytotoxic Test kit (Wako Pure Chemical Industries, Ltd., Japan).

### 2.7. Controlled protein adsorption on surface patterned with UV-light irradiation

UV light ( $\lambda = 185\text{ nm}$ ) (GL15ZH, Sankyo Denki Co. Ltd., 15 W) was irradiated on a poly(hydromethylsiloxane)-treated PDMS surface through a mesh used for transmission electron microscopy (hole 45  $\mu\text{m}$ , bar 40  $\mu\text{m}$ ; Okenshoji Co. Ltd., Tokyo, Japan) for 3 h in air. The UV-irradiated surfaces were then immobilized with the triblock copolymer (119–324) mentioned above.

The surface was exposed to 0.45 g/dL fluorescein isothiocyanate (FITC)-labeled bovine albumin (Sigma Chemicals, St. Louis, MO, USA) in phosphate-buffered solution (PBS) for 30 min and rinsed with PBS and water. The sample was dried in an argon stream and observed using a fluorescent microscope (IX-70, Olympus Co., Tokyo, Japan).

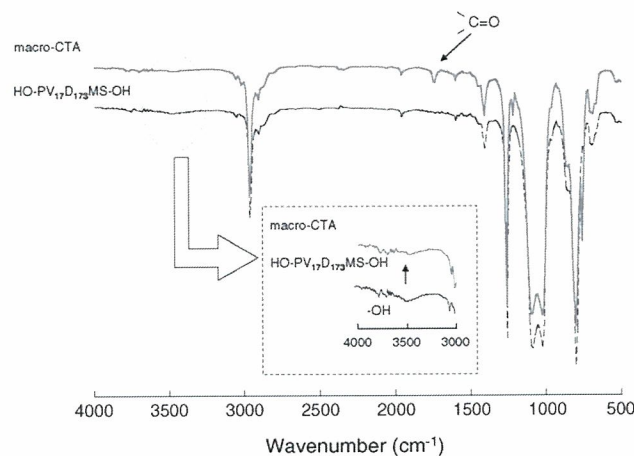


Fig. 2. IR spectra of PV<sub>17</sub>D<sub>173</sub>MS and macro-CTA.

## 3. Results and discussion

### 3.1. Synthesis of triblock copolymers

Hydroxy-terminated poly(dimethylsiloxane) copolymers (HO-PV<sub>*l*</sub>D<sub>*m*</sub>MS-OH) were synthesized by ring-opening polymerization of cyclotetrasiloxane compounds (Scheme 1). The ratio of dimethylsiloxane and vinylmethylsiloxane in the copolymer could be controlled by their ratio in the feed. The molecular weight of the synthesized silicone compounds was measured by SEC-MALS. For HO-PV<sub>17</sub>D<sub>173</sub>MS-OH and HO-PV<sub>32</sub>D<sub>324</sub>MS-OH, the absolute molecular weights were  $(1.43\text{ and }2.68) \times 10^4$ , respectively. Their ratio of apparent molecular weight measured by GPC to absolute molecular weight was 1.4. The absolute molecular weight of HO-PV<sub>53</sub>D<sub>537</sub>MS-OH was calculated at  $4.44 \times 10^4$  from the apparent molecular weight. The molecular weight of HO-PV<sub>53</sub>D<sub>537</sub>MS-OH increased linearly ( $r^2 = 0.99$ ) with an increase in the monomer ratio to M<sub>2</sub><sup>R</sup>D<sub>8</sub>.

4-Cyanopentanoic acid dithiobenzoate, that is, the RAFT agent was reacted with the HO-PV<sub>*l*</sub>D<sub>*m*</sub>MS-OH by condensation. Fig. 2 shows the FT-IR spectra of HO-PV<sub>*l*</sub>D<sub>*m*</sub>MS-OH and that reacted with the 4-cyanopentanoic acid dithiobenzoate. After the reaction, absorption due to the carbonyl group at  $1750\text{ cm}^{-1}$  was observed. The absorption of the hydroxyl group at  $3500\text{ cm}^{-1}$  diminished. Quantitative determination of the condensation was performed by <sup>1</sup>H NMR. In every case, the composition of the RAFT agent was approximately 2 when the molecular weight of the silicone compound determined by SEC-MALS was used.

Living radical polymerization has a great deal of synthetic power in controlling the molecular architecture of polymers and is an exceptionally robust method for producing block or graft copolymers [28,39–41]. The living radical polymerization of MPC recently resulted in the preparation of biocompatible block [35,42–45] and graft copolymers [46,47].

While Ma et al. firstly synthesized a series of diblock and triblock copolymers of PMPC and oligodimethylsiloxane *via* ATRP, the characterization of the block copolymers was not described in detail because of the solubility



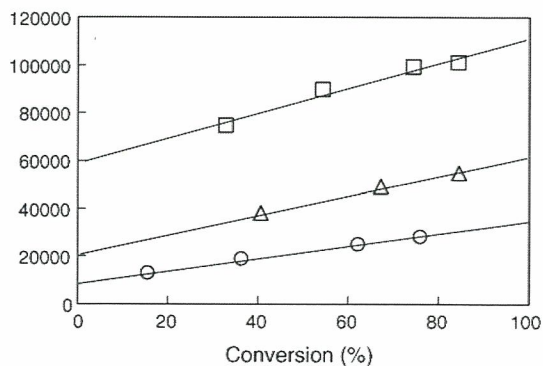


Fig. 3. Dependence of  $M_w$  on conversion in the polymerization of MPC: (○) PMPC-PV<sub>17</sub>D<sub>173</sub>MS-PMPC; (△) PMPC-PV<sub>32</sub>D<sub>324</sub>MS-PMPC; (□) PMPC-PV<sub>53</sub>D<sub>537</sub>MS-PMPC.

difference of the components [42]. We also tried to synthesize macro-initiator for ATRP. However, the decrease in the molecular weight of HO-PV<sub>*l*</sub>D<sub>*m*</sub>MS-OH was observed when HO-PV<sub>*l*</sub>D<sub>*m*</sub>MS-OH was reacted with 2-bromoisobutyryl bromide.

RAFT polymerization of MPC with RAFT agent-capped silicone as a dithioester chain transfer agent (macro-CTA) was then performed in toluene/ethanol (1/1) at 70 °C. Even though macro-CTAs have vinyl groups as side chains, any gelation during polymerization was not observed. Fig. 3 shows the relationship between the molecular weight determined by GPC and the conversion of the MPC polymers. In every polymer system, the GPC results show a single peak and the molecular weight of the block copolymer is linear with conversion. Fig. 4 shows that the monomer consumption followed first order kinetics. The semi-logarithmic plot indicates that polymerization is first order with respect to MPC and implies that the polymer radical concentration remains constant on the polymerization time scale. Table 2 summarizes the characterization of PMPC-PV<sub>*l*</sub>D<sub>*m*</sub>MS-PMPC triblock copolymers with various chain lengths. The degree of polymerization (PD) of the MPC polymer increased with an increase in the ratio of MPC to macro-CTA. The yield of polymerization related with polymerization kinetics and increased with an increase in the molecular weight of macro-CTA. The molecular weight distributions were relatively larger with the

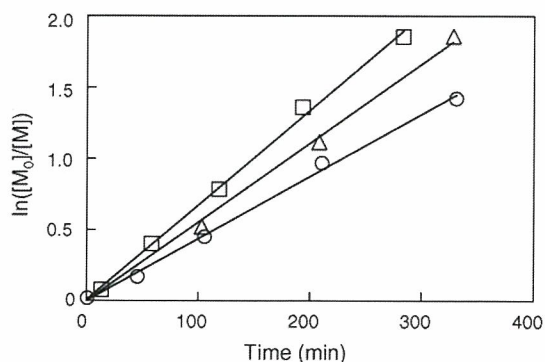


Fig. 4. Kinetics of RAFT polymerization of MPC: (○) PMPC-PV<sub>17</sub>D<sub>173</sub>MS-PMPC; (△) PMPC-PV<sub>32</sub>D<sub>324</sub>MS-PMPC; (□) PMPC-PV<sub>53</sub>D<sub>537</sub>MS-PMPC.

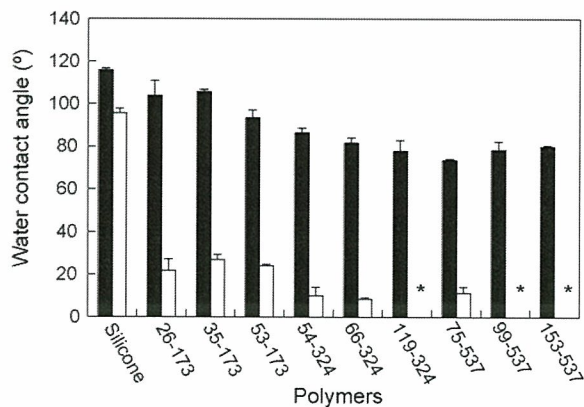


Fig. 5. Water contact angles of native silicone film and that coated with block copolymers: (■) advancing contact angle ( $\theta_A$ ); (□) receding contact angle ( $\theta_R$ ). \* represents spreading of water drop.

higher molecular weights. The ratio of MPC and silicone units was calculated from the phosphorus analysis data. When PV<sub>32</sub>D<sub>324</sub>MS was used as macro-CTA, the composition of the MPC units in a copolymer was higher than that of other macro-CTAs.

### 3.2. Surface modification and characterization of PDMS with triblock copolymers

All copolymers were dissolved in ethanol and coated on silicone films. The water contact angle data was recorded using specimens dried for several hours under reduced pressure before measurement (Fig. 5). The data for the native PDMS was  $\theta_A/\theta_R = 116^\circ/96^\circ$  and did not change by treatment with poly(hydromethylsiloxane). The  $\theta_A$  on the surface coated with the triblock copolymers was recorded at the first addition of water and it gradually decreased with an increase in the composition of the MPC unit in the copolymers. The  $\theta_R$  on the modified surface was decreased dramatically to less than  $30^\circ$ . Particularly, the  $\theta_R$  on a surface coated with copolymers (119–324, 99–537, and 153–537) could not be measured because the water drop spread completely.

The elemental analyses of the polymer-coated silicone surfaces were performed with XPS. In the case of a silicone film coated with the triblock copolymer (66–324), nitrogen and phosphorus peaks were observed at 402.5 and 134.0 eV, respectively (Fig. 6). These were not observed on the native silicone film and were attributed to the phosphorylcholine group in the MPC units. To affect the chemical reaction of surface modification, the triblock copolymer was treated without a Pt catalyst or Si–H treatment. In both cases, the phosphorus and nitrogen signals caused by the MPC polymers were negligible. The surface modification with the triblock copolymers was then performed through hydrosilylation. The XPS phosphorus concentration of the surface-modified silicone films is summarized in Fig. 7. The increment of concentration was caused by an increase in the bulk composition of the MPC unit in the triblock copolymers. Although the block copolymer with a longer central silicone chain (153–537) has longer PMPC chains, the XPS phosphorus concentration on the surface coated with 153–537 was less

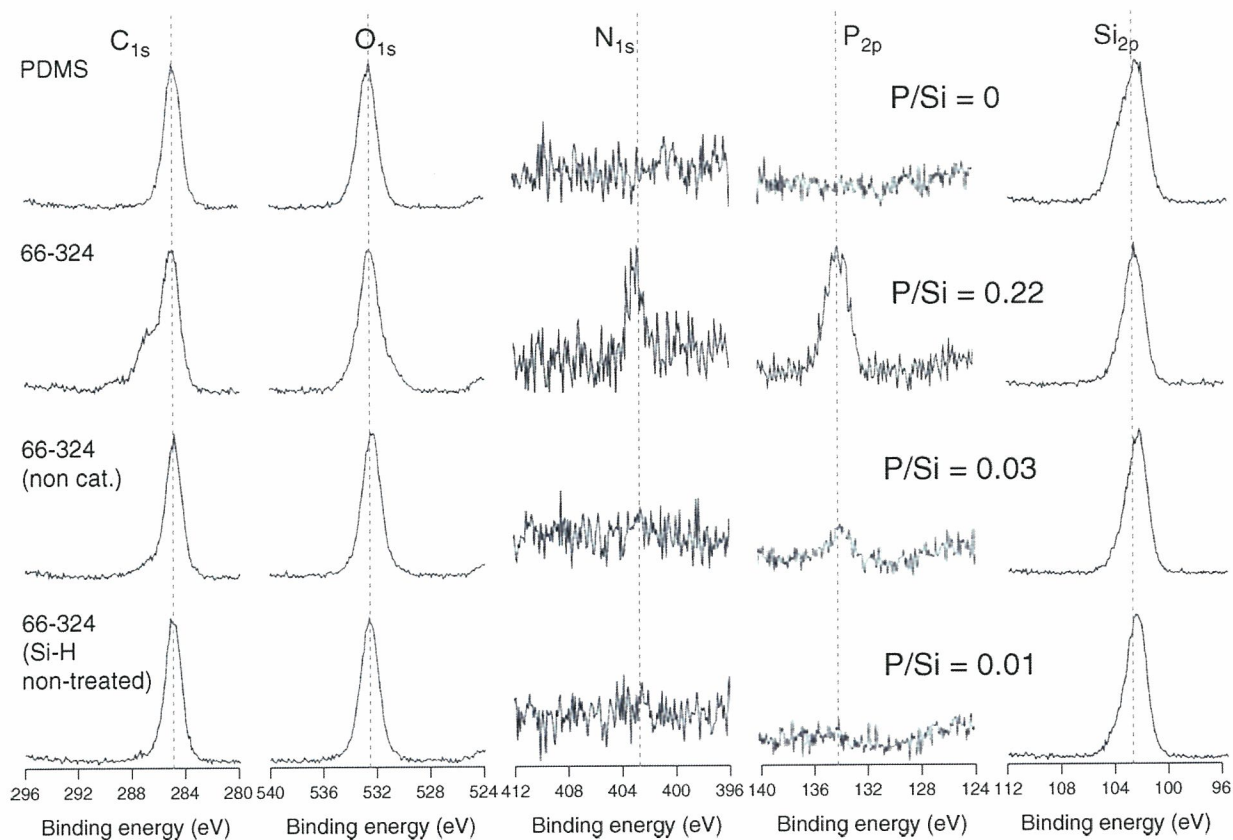


Fig. 6. XPS spectra of native silicone film and that coated with the triblock copolymer (66–324).

than that on the surface coated with 119–324. This result indicates that the central silicone block with high molecular weight reduce the density of PMPC chains on the surface. Sugiyama et al. synthesized poly(MPC-*b*-PDMS) by conventional radical polymerization and surface modification of PDMS with the block copolymer was performed [48]. While the block copolymers improved wettability, the contact angle was still higher than that on comb-shaped polymer brush surface of PMPC [36]. The silicone segments of the block copolymers influenced the mobility of PMPC segments. On the other hand, the PMPC segments of ABA typed block copolymers synthesized in this study were

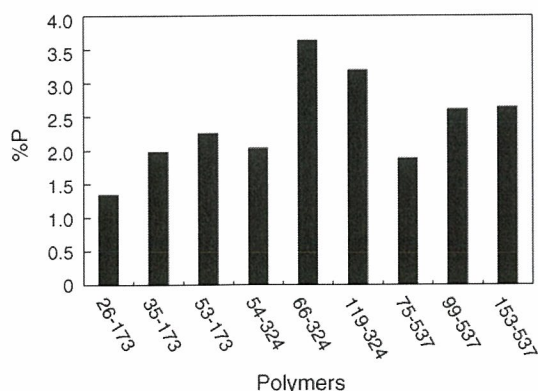


Fig. 7. XPS phosphorus concentration of silicone films modified with PMPC-PV<sub>1</sub>D<sub>m</sub>MS-PMPC triblock copolymers.

free. Highly wettable surfaces were obtained due to the ABA typed structure.

One of the interesting properties of MPC polymers is to produce lower friction and improved boundary lubrication under wet condition [49] and this property is important for making biomedical devices such as, catheters. To clarify the effect of chemical structure of block copolymers on improving boundary lubrication, we measured surface friction of modified surfaces. Fig. 8 shows the friction coefficient of the silicone films coated with triblock copolymers at startup (static) and in the steady (kinetic) conditions in water. The static and kinetic friction coefficients of non-treated silicone film were coefficient  $2.0 \pm 0.4$  and  $1.4 \pm 0.3$ , respectively. These coefficients were significantly reduced by triblock copolymer coatings. The surface friction was decreased with an increase in the ratio of MPC in a copolymer. Even if the 153–537 has long PMPC blocks, the longer silicone block is an obstacle to improve surface lubrication. In the case of the triblock copolymer (119–324)-coated surface, the kinetic friction coefficient was less than 0.01. The surface friction was effectively reduced by coating of optimally sequenced ABA block copolymers as well as “grafting from” typed surface modification [14]. This phenomenon is attributed to the removal of the strong hydrophobic interaction between the PDMS surfaces in water [50] and a similar state of hydrodynamic lubrication.

Moro et al. investigated the effects of the graft polymerization of MPC onto polyethylene surfaces. They clarified that MPC grafting remarkably decreased friction and the amount of wear [51]. The PMPC-PV<sub>1</sub>D<sub>m</sub>MS-PMPC triblock copolymers syn-

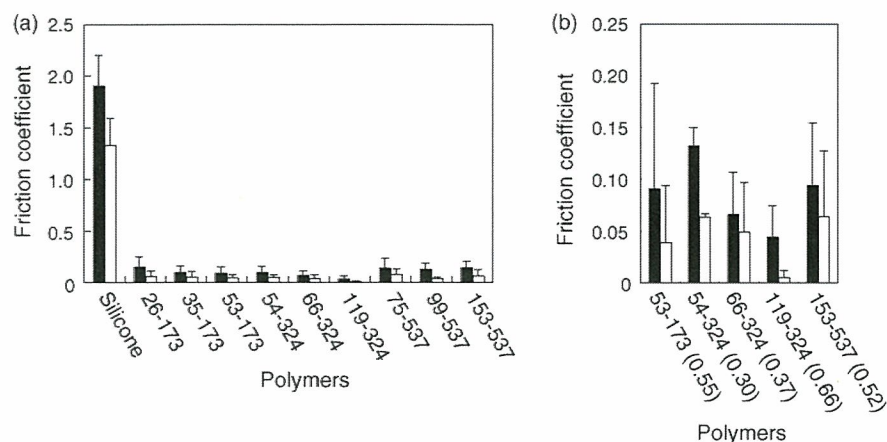


Fig. 8. Friction coefficients of silicone films modified with block copolymers: (■) startup; (□) steady state; (a) all data; (b) selected data for a better reading. The values in parentheses:  $n \times 2/(l + m)$ ,  $\text{PMPC}_n\text{-PV}_l\text{D}_m\text{MS-PMPC}_n$ .

thesized in this study can be chemically introduced on various surfaces through the reactivity of the vinyl group in the central silicone chain.

Fig. 9 shows the results of a continuous friction test on a silicone film and that coated with the triblock copolymer (119–324). The low friction coefficient of a surface coated with the triblock copolymer (119–324) did not change during the determination. This result indicates that surface modification with a block copolymer is stable due to chemical bonding to the substrate. The long-term stability of coating layer and the influence of percentage of vinyl unit will be presented in near future.

### 3.3. Non-fouling behavior on PDMS surface coated with $\text{PMPC-PV}_l\text{D}_m\text{MS-PMPC}$ triblock copolymers

Fig. 10 shows SEM pictures of a polymer surface after contact with human PRP for 60 min. Many platelets adhered and were active on the non-treated silicone surface. In contrast, platelet adhesion was effectively reduced on the PDMS surface coated with the triblock copolymer (119–324). The quantitative result for adherent platelets on various surfaces is summarized in Fig. 11. On every  $\text{PMPC-PV}_l\text{D}_m\text{MS-PMPC}$  triblock copolymer-immobilized surface, the number of adherent platelets was significantly smaller than that on a non-treated silicone surface. Moreover, platelet adhesion was significantly

decreased on the surface coated with 119–324 compared to that coated with 153–537, that is, the surface density of PMPC chains also influenced non-fouling properties. The suppression of platelet adhesion on the block copolymer-coated surfaces is due to the reduction of plasma protein adsorption. In the former literatures [23,24,52], the mechanism of protein adsorption resistance on MPC polymers has been well reported and the property was observed regardless of type of protein. The reduction of albumin adsorption on the surface coated with a triblock copolymer is presented in Fig. 12.

Surface modification with well-defined MPC polymers on a solid surface produced by living radical polymerization has been chiefly reported by Feng et al. [53]. The effect of thickness and density of the PMPC polymer on protein adsorption is also well characterized [54]. Surface samples with various graft densities from 0.06 to 0.39 chains/ $\text{nm}^2$  and chain lengths from 5 to 200 MPC units were prepared. They clarified that the surfaces with high graft densities and high PMPC chain lengths showed dramatic reductions in fibrinogen adsorption. A well-defined surface structure bearing a free end of the polymer chain must be advantageous for obtaining the efficiency of MPC polymers on non-fouling phenomena. The  $\text{PMPC-PV}_l\text{D}_m\text{MS-PMPC}$  triblock copolymer is suitable for fabricating this surface structure by a simple coating process.

Adsorption of FITC-labeled BSA was well controlled on a patterned polymer surface, as shown in Fig. 12. In the region

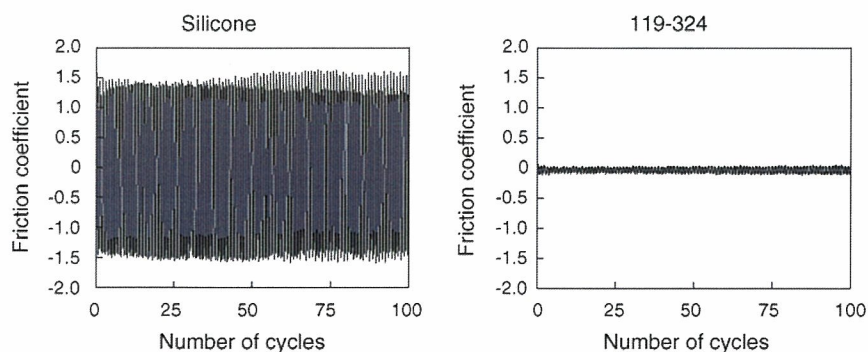


Fig. 9. Continuous friction test for a silicone film and that coated with the triblock copolymer (119–324).

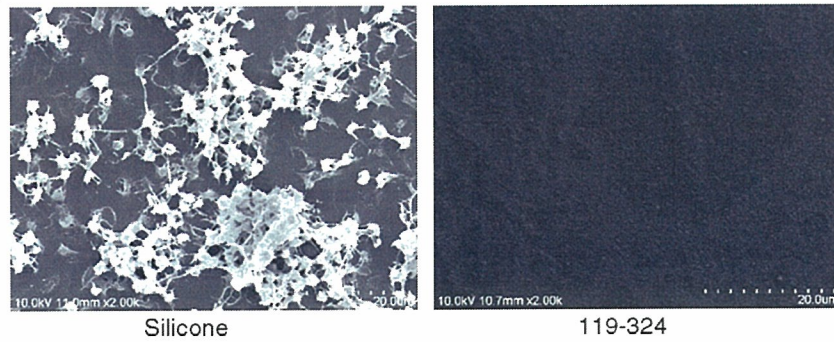


Fig. 10. SEM pictures of polymer surfaces after contact with PRP for 60 min.

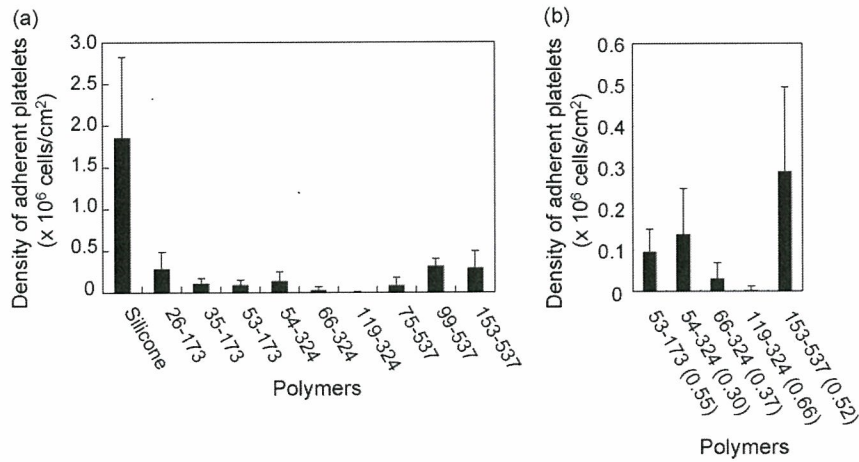


Fig. 11. Surface density of adherent platelets on polymer surfaces in contact with PRP for 60 min: (a) all data; (b) selected data for a better reading. The values in parentheses:  $n \times 2/(l+m)$ ,  $\text{PMPC}_n\text{-PV}_l\text{D}_m\text{MS-PMPC}_n$ .

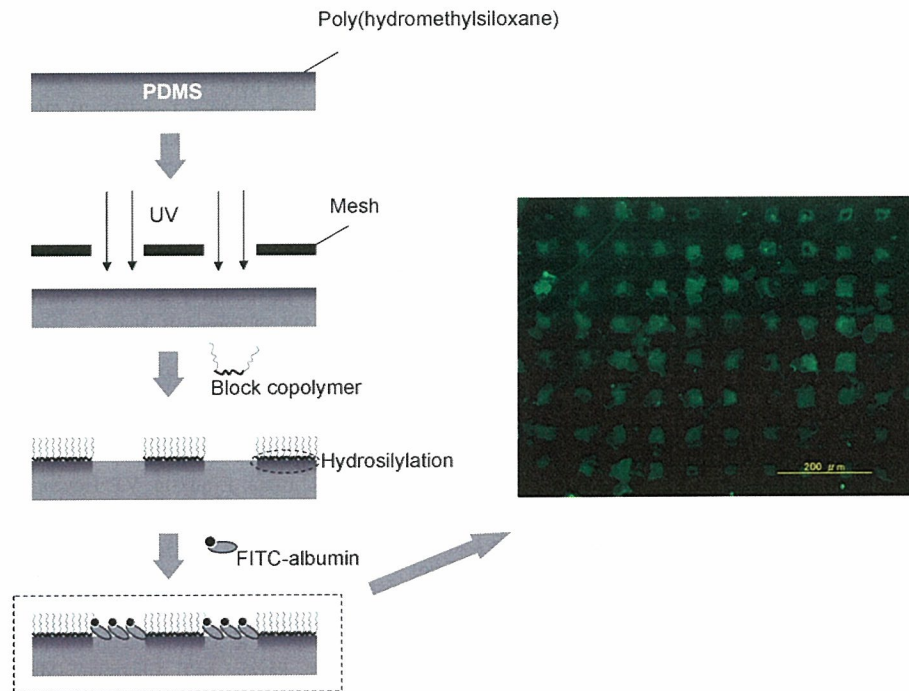


Fig. 12. FITC-albumin adsorption on PDMS surface coated with the triblock copolymer (119–324) with micropatterning after contact with 0.45 g/dL FITC-albumin in PBS for 30 min.

irradiated with UV, no Si–H bond was determined by ATR-FT-IR (data not shown). Fig. 6 shows that surface modification is performed *via* hydrosilylation, that is, Si–H bond is required on the substrate surface. The triblock copolymer (119–324) selectively reacted with the non-UV-irradiated region. The intensity of the surface fluorescence of the UV-irradiated region was significantly high. This indicates that a large amount of BSA was adsorbed on this region. In contrast, BSA adsorption was effectively reduced on the region covered with mesh. The protein adsorption behavior confirmed that the surface modification with block copolymers was performed thorough hydrosilylation. The surface modification with ABA block copolymers can prepare highly defined micropatterns and their potential applicability to biosensor and drug screening development will be demonstrated.

#### 4. Conclusion

For the surface modification of PDMS, PMPC–PV<sub>l</sub>D<sub>m</sub>MS–PMPC triblock copolymers were synthesized *via* RAFT polymerization. Polymerization of each unit was well controlled and the molecular weight distribution was relatively low. The rate of copolymerization of MPC depends on the molecular weight of the macro-CTA. The copolymers were coated on PDMS and chemically bonded *via* hydrosilylation. The surface wettability of the copolymer-immobilized surface was significantly improved compared with that of native PDMS. Copolymers are very effective in reducing the coefficient of friction of the surface. Platelet adhesion and protein adsorption on the PDMS surface coated with triblock copolymers was reduced dramatically. To optimize the sequence of block copolymers is very important because the surface properties coated with the block copolymers depend on both the molecular weight and density of PMPC chains, and RAFT polymerization well works to achieve this process. We also succeeded in controlling the size of the modification area on a microscale and in manipulating protein adsorption on the surface.

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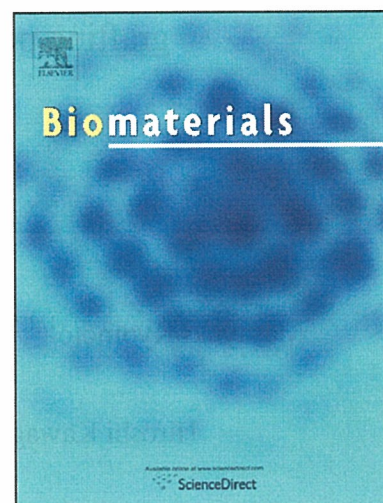
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## Author's Accepted Manuscript

High lubricious surface of Cobalt-Chromium-Molybdenum alloy prepared by grafting poly(2-Methacryloyloxyethyl Phosphorylcholine)

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High lubricious surface of cobalt-chromium-molybdenum alloy prepared by  
grafting poly(2-methacryloyloxyethyl phosphorylcholine)

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**ABSTRACT**

Osteolysis caused by wear particles from polyethylene in artificial hip joints is of great concern. Various bearing couple combinations, bearing material improvements, and surface modifications have been attempted to reduce such wear particles. With the aim of reducing the wear and developing a novel artificial hip joint system, we created a highly lubricious metal bearing material: A 2-methacryloyloxyethyl phosphorylcholine (MPC) polymer was grafted onto the surface of the cobalt-chromium-molybdenum (Co-Cr-Mo) alloy. For ensuring the long-term retention of poly(MPC) on the Co-Cr-Mo alloy, we used a 4-methacryloyloxyethyl trimellitate anhydride (4-META) intermediate layer and photo-induced graft polymerization technique to create a strong bonding between the Co-Cr-Mo substrate and the poly(MPC) chain via the 4-META layer. The Co-Cr-Mo alloy was pretreated with nitric acid and O<sub>2</sub> plasma to facilitate efficient interaction between the 4-META carboxyl group and the surface hydroxyl group on the Cr oxide passive layer of the Co-Cr-Mo alloy. After MPC grafting, the MPC unit peaks were clearly observed in the FT-IR/ATR and XPS spectra of the Co-Cr-Mo surface. Tribological studies with a pin-on-plate machine revealed that surface MPC grafting markedly lowered the friction coefficient. We concluded that the grafted poly(MPC) layer successfully provided high lubricity to the Co-Cr-Mo surface.

Running title: Synthesis of Co-Cr-Mo-g-MPC

## 1. Introduction

The number and prevalence of primary and revision hip and knee joint replacements are substantially increasing worldwide every year [1]. This implies that the quality of artificial joints is becoming increasingly important. Most patients who receive an artificial joint experience a dramatic relief from pain and enjoy a rapid improvement in their quality of life. The most widely used bearing couple in artificial hip joint systems is the combination of an ultra-high molecular weight polyethylene (UHMWPE) acetabular component and a metal femoral component. The cobalt-chromium-molybdenum (Co-Cr-Mo) alloy is one of the most widely used metal bearing materials in artificial joint systems. The Co-Cr-Mo alloy has good mechanical properties, castability, corrosion resistance, and wear resistance, whereas stainless steel and titanium alloys have a disadvantage with regard to corrosion resistance and wear resistance, respectively.

In total hip arthroplasty (THA), osteolysis caused by the wear particles from UHMWPE has been recognized as a serious issue [2–4]. Efforts to decrease these particles have focused on bearing material improvement and the use of combinations other than metal-on-UHMWPE [5–7]. Recently, a metal-on-metal type artificial hip joint system consisting of Co-Cr-Mo acetabular and femoral components has been studied [8,9]. The advantages of the Co-Cr-Mo/Co-Cr-Mo bearings are the absence of the generation of UHMWPE wear debris and decreased wear as compared to that in the case of the Co-Cr-Mo/UHMWPE bearings [10,11]. However, even in the Co-Cr-Mo/Co-Cr-Mo bearings, aseptic loosening induced by wear particles and metallosis remain as serious issues in revision surgeries [12,13]. In addition to metallosis, electrochemical corrosion

and carcinogenesis occurring due to the dissemination of wear particles to the other parts of the body have been reported [14].

In order to reduce such wear particles, improvements in the bearing materials and surface modifications of the Co-Cr-Mo alloy have been attempted [15,16]. Surface coating may reduce the UHMWPE wear without compromising the bulk mechanical properties of the implant materials. Various “hardening treatments” on metal bearing surfaces, such as diamond-like carbon coating, titanium nitride coating and ion implantation have been attempted [17–19]. Although these surface modifications may improve the THA survivorship, the limited THA longevity imposes restrictions for its application in younger patients. Consequently, the possibility of replacing the femoral head alone, in either solid or articular surface replacement form, during revision surgeries of metal-on-metal THA remains an attractive feature of such implants. However, the Co-Cr-Mo alloy or the hardening-treated Co-Cr-Mo alloy may induce damage to the cartilaginous tissue.

On the other hand, previous studies reported that highly lubricious hydrogel polymer used as an artificial cartilage did not damage the against cartilaginous tissue [20,21]. We have recently developed a highly lubricious artificial hip joint system by a “mild treatment” with soft materials. In this treatment, poly(2-methacryloyloxyethyl phosphorylcholine (MPC)) was grafted onto the surface of CLPE (CLPE-g-MPC) [22–24]. MPC is a methacrylate monomer with a phospholipid polar group in a side chain and is used to prepare novel polymer biomaterials, as designed by Ishihara et al. who were inspired by the neutral phospholipids of cell membranes [25]. Many polymers containing the MPC unit are widely used as biomaterials [26–33]. Moreover, various

medical devices have already been developed using poly(MPC) and are being used clinically. The efficacy of MPC polymer as a biomaterial has been well verified [34–36]. Based on the biocompatibility and hydrophilicity of poly(MPC), we have been developing new artificial joints with highly lubricious bearing surfaces that are formed by photo-induced radical graft polymerization.

In this study, we synthesized a highly lubricious metal bearing material in which the MPC polymer was grafted onto the surface of the Co-Cr-Mo alloy (Co-Cr-Mo-g-MPC) for developing a novel artificial hip joint system—artificial femoral head and metal-on-metal (Co-Cr-Mo/Co-Cr-Mo) type—for THA. We also investigated the surface structure and tribological properties of Co-Cr-Mo-g-MPC.

## 2. Materials and Methods

### 2.1. Co-Cr-Mo alloy substrate and pretreatments

The Co-Cr-Mo alloy was supplied by Yoneda Advanced Casting Co., Ltd (Takaoka, Japan). The chemical composition of the Co-Cr-Mo alloy used in this study is listed in Table 1. This alloy was manufactured according to the ASTM F75 standard specification for Co-28Cr-6Mo alloy [37]. The Co-Cr-Mo samples were polished so that the average surface roughness ranged between 0.01–0.02  $\mu\text{m}$ .

The polished Co-Cr-Mo samples were washed with acetone, and then immersed in 35vol% nitric acid at room temperature for 35 min according to the ASTM F86-04 standard [38]. This treatment