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3 gamma-ray irradiated at 50 kGy in N₂ gas and annealed at 120°C in N₂ gas for crosslinking. After
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6 cooling, the cross-linked polyethylene (CLPE) specimens were machined from this bar stock.

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8 MPC grafting onto the CLPE surface was performed as described in previous studies.⁴³⁻⁴⁵ The
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12 CLPE specimens were immersed in an acetone solution containing 10 mg/mL benzophenone for 30
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15 s and then dried in the dark at room temperature to remove the acetone. MPC was dissolved in
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18 degassed pure water to a concentration of 0.5 mol/L. The benzophenone-coated CLPE samples
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22 were immersed in the aqueous MPC solution. Photoinduced graft polymerization on the CLPE
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25 surface was carried out using UV irradiation with an intensity of 5 mW/cm² at 60°C for 90 min.
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28 After the polymerization, the CLPE-g-MPC samples were removed from the solution, washed with
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31 pure water and ethanol, and dried.

32 33 34 35 36 37 **Articular cartilage from porcine ankle joint**

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40 Using a surgical hand corer or surgical saw, articular cartilage specimens were harvested from the
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43 flat part of the ankle joint of the fresh frozen porcine tibia (ages 6–9 months). Pin-type articular
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46 cartilage specimens were shaped as cylinders with a height of 5 mm and diameter of 9 mm, and they
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49 had approximately 1 mm of cartilage layer and subcondral bone used for mounting. Throughout
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52 the procedure, the articular cartilage surface was hydrated regularly with Dulbecco's
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55 phosphate-buffered saline (PBS, pH 7.4, ion strength = 0.15 M; Immuno-Biological Laboratories
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58 Co., Ltd., Takasaki, Japan). All the articular cartilage specimens were then stored in Dulbecco's
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61 PBS and frozen at -80°C.⁴⁶

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6 **Surface analysis by Fourier-transform infrared spectroscopy, X-ray photoelectron**
7 **spectroscopy, and water-contact angle measurement**
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12 The functional group vibrations of the Co-Cr-Mo alloy surfaces before and after the MPC grafting
13 were examined by Fourier-transform infrared (FT-IR) spectroscopy with attenuated total reflection
14 (ATR) equipment. The FT-IR/ATR spectra were obtained using an FT-IR analyzer (FT/IR615,
15 JASCO Co. Ltd., Tokyo, Japan) for 32 scans (1.2 s/scan) over the range of 800 to 2000 cm^{-1} at a
16 resolution of 4.0 cm^{-1} .
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28 The surface elemental conditions of the Co-Cr-Mo alloy before and after the MPC grafting were
29 analyzed by X-ray photoelectron spectroscopy (XPS). The XPS spectra were obtained using an
30 XPS spectrophotometer (AXIS-HSi165, Kratos Analytical Ltd., Manchester, UK) equipped with a
31 15-kV Mg- $K\alpha$ radiation source at the anode. The take-off angle of the photoelectrons was
32 maintained at 90°. Five scans (approximately 260 to 425 s/scan depending on the atomic signal
33 strength) were taken for each sample.
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47 The static-water contact angles on the Co-Cr-Mo surfaces that were subjected to different types of
48 pretreatments before and after the MPC grafting were measured by the sessile drop method using an
49 optical bench-type contact angle goniometer (Model DM300, Kyowa Interface Science Co., Ltd.,
50 Saitama, Japan). Drops of purified water (1 μL) were deposited on the Co-Cr-Mo-g-MPC surface,
51 and the contact angles were directly measured with a microscope after 60 s of dropping, according to
52 the ISO 15989 standard.⁴⁷ Measurements were repeated six times for each sample, and the average
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3 values were considered as the contact angles.
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8 9 **Cross-sectional observation by transmission electron microscopy**

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11 A cross-section of the poly(MPC) layer on the Co-Cr-Mo surface was observed using a
12 transmission electron microscope (TEM) and by energy dispersive X-ray (EDX) spectroscopy.
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15 The specimens were pre-coated with an aluminum film using a focused ion beam (FIB) system to
16 prevent charging. After pre-coating, a thin film of the samples was prepared by the FIB technique
17 using an FB-2000A (Hitachi High-Technologies Co., Tokyo, Japan) FIB system. The samples
18 were thinned to electron transparency by a low gallium ion beam current. The thin film thus
19 prepared was positioned onto a copper TEM mesh grid. TEM observations were then recorded
20 using an HF-2000 electron microscope (Hitachi High-Technologies Co.) at an acceleration voltage
21 of 200 kV. EDX spectra were analyzed on a cross-section of the untreated Co-Cr-Mo sample and
22 the Co-Cr-Mo-g-MPC sample obtained with 0.50 mol/L MPC concentrations and a 90-min
23 photoirradiation time using a Sigma EDX attachment (Kevex Instruments, Inc., Valencia, CA, USA)
24 at an acceleration voltage of 200 kV. The probe size of the electron beam was maintained at 1 nm.
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53 **Friction test**

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55 The coefficients of dynamic friction between the pins fabricated from various materials and the
56 untreated Co-Cr-Mo or Co-Cr-Mo-g-MPC (obtained with 0.50 mol/L MPC concentrations and a
57 90-min photoirradiation time) plates were measured using a pin-on-plate machine (Tribostation 32;
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3 Shinto Scientific Co., Ltd., Tokyo, Japan). Each pin was a cylinder measuring 5 mm in height and
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6 9 mm in diameter and used to prepare six sample pieces. The friction tests were performed at room
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9 temperature with a load of 0.98 N, sliding distance of 25 mm, and frequency of 1 Hz for a maximum
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12 of 100 cycles.⁴⁸ Pure water was used as a lubricant. The mean coefficients of dynamic friction
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15 were determined by averaging five data points from the 100 (96–100) cycle measurements.
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22 RESULTS

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25 Fig. 2 shows the FT-IR/ATR spectra of the Co-Cr-Mo sample and that of photoirradiated grafting
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27 of MPC under 0.50-mol/L MPC concentration and 90-min photoirradiation time. Absorption
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29 peaks were not observed for the Co-Cr-Mo sample before the MPC graft polymerization in the
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31 wavenumber range of 800 to 2000 cm^{-1} . In contrast, absorption peaks were newly observed only
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33 for the Co-Cr-Mo-g-MPC samples. The peaks at 1720, 1550, and 1460 cm^{-1} are attributed to C=O
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35 and -CH₂- in the MPSi and poly(MPC) graft chains. The peaks at 1180, 1040, 700, and 630 cm^{-1}
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37 are attributed to the trimethoxysilane group in the MPSi unit.⁴⁹ The peaks at 1240, 1080 and 970
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39 cm^{-1} are attributed to the -N⁺(CH₃)₃ and phosphate groups in the MPC unit.⁴⁴
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50 In the XPS spectra of the binding energy region of the silicon (Si_{2p}), nitrogen (N_{1s}), and
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52 phosphorous (P_{2p}) electrons, peaks appeared in the case of Co-Cr-Mo-g-MPC; however, they were not
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54 observed in the case of Co-Cr-Mo (data not shown). The peak at 103 eV was attributed to the Si₂O₃
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56 or SiO₂ in the trimethoxysilane group in the MPSi unit. The peaks at 403 and 134 eV were attributed
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58 to the -N⁺(CH₃)₃ and phosphate groups, respectively. These peaks reflect the phosphorylcholine
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3 present in the MPC units. Fig. 3 shows the Si, N, and P concentrations of the Co-Cr-Mo-g-MPC
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5 surface as a function of the photoirradiation time during polymerization for various MPC
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7 concentrations in feeds. Both the N and P concentrations in the Co-Cr-Mo-g-MPC surface increased
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9 with the photoirradiation time. In the case of higher MPC concentrations, when the photoirradiation
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11 time was greater than 90 min, the N and P concentrations became almost constant above 5.0 atom%.
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13 These values were almost equivalent to the theoretical elemental composition (N = 5.3 atom%, P = 5.3
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15 atom%) of poly(MPC). As a trade-off, the Si concentration at the Co-Cr-Mo-g-MPC surface
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17 decreased with an increase in the photoirradiation time.
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28 Fig. 4 shows the static-water contact angle on the Co-Cr-Mo-g-MPC surface as a function of the
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30 photoirradiation time during polymerization with various MPC concentrations in feeds. The
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32 static-water contact angle on the untreated Co-Cr-Mo surface before the MPC grafting was
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34 approximately 80°. The static-water contact angle on the Co-Cr-Mo-g-MPC surface decreased
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36 markedly with an increase in the photoirradiation time and the MPC concentration. When the
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38 photoirradiation time and MPC concentration were greater than 90 min and 0.50 mol/L, respectively,
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40 the static-water contact angle became constant at a low value of 20°.
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50 Fig. 5 shows the cross-sectional TEM images of Co-Cr-Mo-g-MPC obtained with various MPC
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52 concentrations and a 90-min photoirradiation time. In the Co-Cr-Mo-g-MPC, a 10–360 nm-thick
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54 poly(MPC) layer was clearly observed on the surface of the Co-Cr-Mo substrate. The thickness of
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56 the poly(MPC) layer increased with the MPC concentration during polymerization. At an MPC
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58 concentration of 0.50 mol/L, the thickness of the poly(MPC) layer was greatest, i.e., 200 nm.
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3 These results indicate that the length of the poly(MPC) chain (thickness of the poly(MPC) layer) can
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5 be controlled by adjusting the MPC concentration during polymerization. This is explained by the
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7 fact that the length of the polymer chains produced in a radical polymerization reaction generally
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9 correlates with the MPC concentration.
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15 Fig. 6 shows the EDX spectra of the untreated Co-Cr-Mo and Co-Cr-Mo-g-MPC obtained with a
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17 0.5-mol/L MPC concentration and a 90-min photoirradiation time. In spectra (P1) and (P3) of the
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19 substrate of the untreated Co-Cr-Mo and Co-Cr-Mo-g-MPC, strong peaks were observed at 0.8, 2.3,
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21 5.4, 6.0, 6.9, and 7.7 keV. These peaks are attributed to the Co, Cr, and Mo atoms in the Co-Cr-Mo
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23 substrate. In spectrum (P2) of the surface of the untreated Co-Cr-Mo, a peak was observed at 0.5
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25 keV. This peak is attributed to the O atom in the metal oxide layer of the Co-Cr-Mo. In spectrum
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27 (P4) of the intermediate layer of the Co-Cr-Mo-g-MPC, peaks were observed at 0.5 and 1.7 keV.
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29 These peaks are attributed to the O and Si atoms in the intermediate layer between the silane of the
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31 MPSi and the metal oxide of the Co-Cr-Mo. In spectra (P4) and (P5) of the intermediate layer and
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33 the poly(MPC) layer of the Co-Cr-Mo-g-MPC, a significant peak attributed to the P atom was
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35 observed at 2.0 keV. This peak is mainly attributed to the MPC units. Several spectra exhibited
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37 peaks at 1.5, 8.0, and 8.9 keV. In these cases, the peaks are attributed to the Al and Cu atoms of the
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39 Aluminum coating for the preparation of the TEM observation specimen and/or the copper TEM
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41 mesh grid.
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Fig. 7 shows the coefficients of dynamic friction of the sliding couples, namely, untreated Co-Cr-Mo, CLPE, CLPE-g-MPC, and articular cartilage pins sliding against the untreated

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3 Co-Cr-Mo and Co-Cr-Mo-g-MPC plates. The Co-Cr-Mo/Co-Cr-Mo and CLPE/Co-Cr-Mo
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6 couples showed a high friction coefficient of approximately 0.19 and 0.14 in the initial 10 cycles;
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9 especially, the value of the Co-Cr-Mo/Co-Cr-Mo couple increased and reached approximately 0.41
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12 in the 100 cycles. After the friction test, some scratches parallel to the sliding direction were
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15 clearly observed in the Co-Cr-Mo/Co-Cr-Mo bearing area. The CLPE-g-MPC/Co-Cr-Mo couples
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18 showed a low friction coefficient of about 0.05 for both 10 and 100 cycles. This corresponds to an
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21 approximately 70% reduction when compared to the coefficients of untreated CLPE/Co-Cr-Mo
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24 couples. The coefficients of dynamic friction of all types of pins sliding against the
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27 Co-Cr-Mo-g-MPC couples decreased drastically as compared with those of untreated Co-Cr-Mo
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30 couples. The degree of reduction in the coefficient was approximately 90% (80 to 99%) for both
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33 10 and 100 cycles. In particular, in the CLPE-g-MPC/Co-Cr-Mo-g-MPC couple, the poly(MPC)
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36 layer sliding against the poly(MPC) layer showed the lowest friction coefficient of approximately
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39 0.005, and this value was almost steady during the experiment. The friction coefficient of the
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42 cartilage/Co-Cr-Mo couple increased gradually and reached approximately 0.09 in the 100 cycles.
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45 The friction coefficient of the cartilage/Co-Cr-Mo-g-MPC couple was approximately 0.006 in the
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48 100 cycles and it remained almost steady. This was much lower than the friction coefficient of the
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51 cartilage/Co-Cr-Mo couple.
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DISCUSSION

In this study, with the aim of reducing wear, a super-lubricious Co-Cr-Mo alloy surface by

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3 poly(MPC) grafting was prepared for its application to artificial joints. Several important issues are
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5 involved in the long-term retention of the benefits of poly(MPC) used in artificial joints under
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7 variable and multidirectional loads: strong bonding between the poly(MPC) and the Co-Cr-Mo
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9 surface, high mobility of the free end groups of the poly(MPC) layer, and a high density of the
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11 introduced poly(MPC). Taking these issues into consideration, the MPSi intermediate layer and
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13 the photoinduced radical graft polymerization technique were used to obtain covalent bonding
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15 between the Co-Cr-Mo substrate and the poly(MPC) chain via the MPSi layer.
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25 MPSi binds to the Co-Cr-Mo substrate by a condensation reaction in two steps (Fig. 1). In the first
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27 step, the MPSi is hydrolyzed (activated) and in the second step, the hydrolyzed silane molecule binds
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29 to the surface by an Si-O-metal (M) bond, forming branched hydrophobic siloxane bonds,
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31 Si-O-Si.^{37,49} The hydrolyzed silane molecule has three -OH groups that can react with the -OH
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33 groups of the surface metallic oxide layer to form siloxane bonds covalently. The peaks at 1180 and
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35 1040 cm^{-1} in the FT-IR/ATR spectrum of the Co-Cr-Mo-g-MPC surface were attributed to Si-O-Si
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37 and Si-O-M, respectively (Fig. 2), and these were observed after the MPC grafting. This suggests
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39 that the trimethoxysilane group of MPSi binds to the metallic oxides with a stable covalent binding
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41 even when the polymerization of MPC was carried out. This MPSi (and/or poly(MPC-co-MPSi))
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43 layer(s) and the Co-Cr-Mo substrate might contribute to the stable polymer/metal interface.⁵⁰
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57 Fig. 3 shows the Si, N, and P concentrations of the Co-Cr-Mo-g-MPC surface obtained with a
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59 0.5-mol/L MPC concentration and a 90-min photoirradiation time. The concentrations became
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almost constant at high values of 5.3 and 5.1 atom%, respectively. These values were almost

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3 equivalent to the theoretical elemental composition of poly(MPC). In addition, the static-water
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5 contact angle of the Co-Cr-Mo-g-MPC surface became constant at a low value of 20°, showing a
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7 highly hydrophilic nature. The peak attributed to Si atoms was observed in the intermediate layer
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9 between the poly(MPC) layer and Co-Cr-Mo substrate only, as shown in Fig. 6. Therefore, it was
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11 assumed that the poly(MPC) chain was grafted and that it extended from the methacrylate on the
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13 MPSi. The hydrophilic layer was formed with the poly(MPC) chain, which attained high mobility,
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15 and the poly(MPSi) chain existed as the immobilized end-group of the poly(MPC) graft chains.
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25 In Fig. 3, both the N and P concentrations in the Co-Cr-Mo-g-MPC surface attributed to
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27 poly(MPC) increased with the MPC concentration during polymerization. In addition, in the TEM
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29 images shown in Fig. 5, the thickness of the poly(MPC) layer increased with the MPC concentration.
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31 When the poly(MPC) layer has a brush-like structure, the layer thickness may correlate with the
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33 molecular weight of the grafted poly(MPC). The high-density poly(MPC) graft chains in the
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35 Co-Cr-Mo-g-MPC are assumed to exhibit a brush-like structure.^{24,51} It is generally well known that
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37 the reaction rate of radical polymerization is extremely high.⁵² In this study, the length (molecular
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39 weight) of the poly(MPC) graft chains was assumed to be successfully controlled by the MPC
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41 concentration used for polymerization as a feed solution. This indicates that the length of the
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43 poly(MPC) chain grafted on the Co-Cr-Mo surface increased with the MPC concentration in feed.⁴⁵
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57 The previous study by the authors reported that the density of the poly(MPC) chains on the
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59 surface of the CLPE prepared by photoinduced radical polymerization gradually increased with the
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irradiation time. The study also showed that the entire surface of the CLPE was coated using

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3 polymerization times longer than 45 min with almost the same thickness as that of the poly(MPC)
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6 layer for longer irradiation times (100 to 200 nm).⁴⁴ In this study, both the N and P concentrations
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9 in the Co-Cr-Mo-g-MPC surface attributed to poly(MPC) increased with the photoirradiation time.
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12 When the MPC concentration was greater than 0.5 mol/L, the N and P concentrations of the
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15 Co-Cr-Mo-g-MPC surface increased to approximately 5.3 atom%, which was almost equivalent to
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18 the theoretical elemental composition of poly(MPC). In addition, the Co-Cr-Mo-g-MPC surface
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21 obtained with a 0.5-mol/L MPC concentration and a 90-min photoirradiation time retained the
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24 uniform poly(MPC) layer with a thickness of 200 nm, as reported in the previous study. These
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27 observations indicate that irradiation time control is essential to obtain a high-density poly(MPC)
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30 layer.⁴⁴
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34 The coefficients of dynamic friction of various bearing couples obtained in previous studies are
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36 summarized in Table 2. In Fig. 7, the Co-Cr-Mo/Co-Cr-Mo couple shows a friction coefficient of
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38 approximately 0.19, which is as high as that described in previous studies.^{41,53} The
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41 CLPE/Co-Cr-Mo couple also shows a friction coefficient of approximately 0.14, as high as that
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44 described in previous studies.^{41,54,55} In contrast, the Co-Cr-Mo-g-MPC surface with respect to each
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47 material shows an extremely low friction coefficient as compared to that of the untreated Co-Cr-Mo
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50 surface. Since MPC is highly hydrophilic and poly(MPC) is water soluble, the water contact angle
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53 of the Co-Cr-Mo-g-MPC surface was lower than that of the untreated Co-Cr-Mo surface, as shown
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56 in Fig. 4. Consequently, the grafted poly(MPC) layer successfully provided high lubricity in the
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59 form of “surface gel hydration lubrication” to the Co-Cr-Mo surface (Fig. 7).⁵⁶
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3 Various factors such as the type of bearing material, surface roughness, homogeneity of the
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5 surface, and chemical composition affect the lubricity of artificial joints.⁵⁷ In the case of
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7 Co-Cr-Mo-g-MPC, the lubricity changes depending on the ambient *in vitro* and *in vivo* conditions.
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10 The previous study reported that the hydrogel cartilage surface is assumed to have a brush-like
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12 structure: a part of the proteoglycan aggregate brush is bonded with the collagen network on the
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14 cartilage surface.⁵⁶ The bearing surface with poly(MPC) in artificial hip joints is assumed to have a
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16 brush-like structure similar to that of articular cartilage. CLPE-g-MPC/Co-Cr-Mo-g-MPC or
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18 cartilage/Co-Cr-Mo-g-MPC bearing couples can therefore be regarded to mimic the natural joint
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20 cartilage *in vivo*. The friction coefficient of cartilage/stainless steel (SUS) pin-on-plate ranges from
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22 0.01 to 0.05,⁵⁸ and that of cartilage/cartilage pin-on-plate is 0.02,⁵⁹ as shown in Table 2. In this
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24 study, it was found that CLPE-g-MPC/Co-Cr-Mo-g-MPC or cartilage/Co-Cr-Mo-g-MPC bearing
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26 couples mimic a natural joint, showed low friction (friction coefficient was approximately 0.01), as
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28 low as that of cartilage/SUS or cartilage/cartilage. Hence, it was considered that the
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30 Co-Cr-Mo-g-MPC surface is excellent for the femoral head articulating cartilage, because the
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32 cartilage/Co-Cr-Mo-g-MPC bearing couples showed a constant low friction coefficient of 0.006.
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34 We expect that the hemi-arthroplasty with the Co-Cr-Mo-g-MPC femoral head bearing will be
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36 promising to preserve acetabular cartilage and extend the duration before THA in young patients.
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56 On the other hand, in the previous study, the CLPE-g-MPC/Co-Cr-Mo-g-MPC prepared by the
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58 adsorption of the polymer to the substrate, termed as the “grafting to” method bearing couples
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60 showed high friction (friction coefficient was 0.12).⁴¹ The poly(MPC) on Co-Cr-Mo used in this

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3 study might have a high density because the polymerization method used was surface-initiated graft
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6 polymerization, termed as the “grafting from” method, in which the monomers are polymerized
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9 from initiators or comonomers, whereas the poly(MPC) on Co-Cr-Mo prepared by the “grafting to”
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12 method might have a low density.^{34,35} Fig. 8 shows the images of high-density grafted
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15 poly(MPC)/low-density grafted poly(MPC) and high-density grafted poly(MPC)/high-density
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18 grafted poly(MPC) bearing interfaces. The high-density grafted poly(MPC)/high-density grafted
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21 poly(MPC) bearing interface shows a remarkably lower friction than the high-density grafted
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24 poly(MPC)/low-density grafted poly(MPC) bearing interface.⁶⁰ Fukuda et al. reported that the
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27 friction of the bearing couple was higher in low-density polymer brushes than in high-density ones.⁶¹
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30 Therefore, it is assumed that a bearing couple with low-density poly(MPC) brushes may cause high
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33 friction by stick-slip motion with interpenetration, as shown in Fig. 8(a).^{60,62} In contrast,
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36 high-density poly(MPC) fabricated by the “grafting from” method may attain low friction, such as
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39 that in the case of “super-lubricity,” owing to resistance to interpenetration by volume effects
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42 resulting from chain mobility. The reduction in friction may contribute to the improvement in
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45 anti-wear properties.¹⁹⁻²¹ Although a hip joint simulator test is necessary to examine tribological
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48 advantages in human body environments, a super-lubricious metal-bearing material would enable
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51 the development of a novel biocompatible artificial hip joint system—artificial femoral head for
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54 partial hemi-arthroplasty and metal-on-polymer/metal type for THA.
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CONCLUSION

We prepared a super-lubricious metal-bearing material for application as a novel artificial hip joint system: poly(MPC) was grafted onto the surface of a Co-Cr-Mo alloy by employing an MPSi intermediate layer and by using the photoinduced radical graft polymerization technique. The thickness and density of the grafted poly(MPC) layer increased with the MPC concentration and photoirradiation time, respectively. In conclusion, the grafted poly(MPC) layer successfully provided super-lubricity to the Co-Cr-Mo surface, and the CLPE-g-MPC/Co-Cr-Mo-g-MPC or cartilage/Co-Cr-Mo-g-MPC bearing interface, which mimicked a natural joint, showed an extremely low friction coefficient of 0.01, a value that is as low as that of a natural cartilage interface.

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