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3 CLPE-g-MPC are discussed in terms of the characteristics of the MPC polymer layer.
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8 9 **MATERIALS AND METHODS**

10 11 **Chemicals**

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15 Benzophenone and acetone were purchased from Wako Pure Chemical Industries, Ltd (Osaka,
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18 Japan). MPC was synthesized industrially using the method reported by Ishihara, et al.¹⁴ and was
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21 supplied by Ai Bio-Chips Co., Ltd (Tokyo, Japan).
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26 27 **MPC graft polymerization**

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31 Compression-molded UHMWPE (GUR1020 resin; Poly Hi Solidur Inc., IN, USA) bar stock was
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34 gamma-irradiated with 50 kGy in N₂ gas and annealed at 120°C for 7.5 h in N₂ gas for cross-linking.
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37 The CLPE specimens were machined from this bar stock after cooling. The specimens were
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40 immersed in an acetone solution containing 10 mg/mL benzophenone for 30 s and then dried in the
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43 dark to remove acetone at room temperature. The amount of benzophenone adsorbed on the
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46 surface was determined by ultraviolet spectroscopy to be 3.5×10^{-11} mol/cm² using a previously
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49 described method.²¹ The MPC monomer was dissolved in degassed pure water to a concentration
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52 of 0.5 mol/L. The CLPE specimens coated with benzophenone were immersed in the aqueous
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55 MPC solution. The photo-induced graft polymerization on the CLPE surface was carried out with
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58 ultraviolet irradiation of 5 mW/cm² for 10 to 360 min at 60°C using a Toshiba D-35 filter that
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permitted the passage of ultraviolet light with a wavelength of 350 ± 50 nm only. After the

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3 polymerization, the CLPE-g-MPC specimens were removed, washed with pure water and ethanol,
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6 and then dried. The CLPE-g-MPC specimens were gamma-sterilized with a dose of 25 kGy under
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9 N₂ gas.

10 11 12 13 14 15 **Surface analysis by using XPS, water-contact angle measurement, and FT-IR/ATR**

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18 The surface elemental conditions of the CLPE before and after MPC grafting were analyzed by
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21 X-ray photoelectron spectroscopy (XPS). The XPS spectra were obtained using an AXIS-HSi165
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24 spectrophotometer (Kratos Analytical Ltd., UK) equipped with an Mg-K α radiation source at 15 kV
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27 at the anode. The take-off angle of the photoelectrons was maintained at 90 degrees. Five scans
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30 were taken for each sample.

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34 The static water-contact angle of the CLPE-g-MPC with various photo-polymerization periods
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37 was measured by a sessile drop method using an optical bench-type contact angle goniometer
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40 (Model DM300; Kyowa Interface Science Co., Ltd., Saitama, Japan). Drops of purified water (1
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43 μ L) were deposited onto the surface of the CLPE-g-MPC, and the contact angles were directly
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46 measured with a microscope after each dropping (60 s), according to the ISO 15989 standard.²²
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49 Fifteen replicate measurements were performed on each sample, and the contact angle values were
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52 averaged.

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56 The functional-group vibrations of the CLPE-g-MPC surface with various photo-polymerization
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59 periods were examined by Fourier-transform infrared (FT-IR) spectroscopy with attenuated total
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reflection (ATR) equipment. The measurements were performed over a range of 800 to 2000 cm⁻¹

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3 by using an FT-IR analyzer (Perkin-Elmer FT-IR 1650; Perkin-Elmer Corp., MA, USA) at a
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6 resolution of 4.0 cm^{-1} for 100 scans.
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9 The relative amount of grafted MPC polymer unit on the CLPE surface was evaluated by
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12 quantification of the phosphate (P–O) group that is contained within the structure of the MPC unit.
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15 The relative amount of phosphate group was defined as the P–O group index, and was calculated as
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18 follows.
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$$20 \text{ P–O group index} = (1080\text{ cm}^{-1}\text{ peak intensity}) / (1460\text{ cm}^{-1}\text{ peak intensity})$$

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31 **Cross-section of CLPE-g-MPC observed with TEM**

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34 A cross-section of the MPC polymer layer on the CLPE-g-MPC surface produced by various
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37 photo-polymerization periods was observed with a transmission electron microscope (TEM). The
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40 specimens (2 pieces for each irradiation time) were first embedded in epoxy resin, stained with
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43 ruthenium oxide vapor at room temperature, and then sliced into ultra-thin films (approximately
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46 100-nm thick) by using a Leica Ultra Cut UC microtome (Leica Microsystems, Ltd., Wetzlar,
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49 Germany). A JEM-1010 electron microscope (JEOL, Ltd., Tokyo, Japan) was used for the TEM
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52 observation at an acceleration voltage of 100 kV.
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56 **Hip simulation wear test**

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The inner and outer diameters of the CLPE-g-MPC cups used in the hip joint simulator were 26

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2 mm and 52 mm, respectively. For each irradiation time (0, 23, 45, 90, and 180 min), 4 pieces were
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4 prepared. The wear test was performed using a 12-station hip joint simulator (MTS system Corp.,
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6 MN, USA). A 26-mm Co-Cr-Mo alloy femoral ball component (Japan Medical Materials Corp.,
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8 Osaka, Japan) was used as an acetabular component. A mixture of 25% bovine serum, 20 mM/L
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10 of ethylenediaminetetraacetic acid (EDTA), and 0.1% sodium azide was used as lubricant, according
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12 to the ISO 14242-1 standard.²³ The lubricant was replaced every 0.5×10^6 cycles. Walks,
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14 simulating a physiologic loading curve (Paul-type) with double peaks of 1793 and 2744 N (183 and
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16 280 kgf) loads, were applied with multidirectional (biaxial and orbital) motion of 1 Hz frequency.
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18 The wear was determined by weighing the polyethylene cups. Load-soak controls ($n = 2$) were
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20 used to compensate for fluid absorption by the wear specimens.²⁴ The weights of the cups were
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22 measured every 0.5×10^6 cycles. The testing continued until a total of 3.5×10^6 cycles were
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24 completed.
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41 In order to evaluate the net wear, corrected for any influence from plastic deformation, a
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43 melt-recovery operation was performed on selected samples of both CLPE and CLPE-g-MPC cups
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45 after the simulator tests, according to the method of Muratoglu, et al.²⁵ The cups were melted at
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47 150°C in a vacuum and allowed to cool down to the room temperature. The surface features of the
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49 bearing surfaces of the cups were observed with a confocal laser scanning microscope (OLS1200;
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51 Olympus Corp., Tokyo, Japan).
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RESULTS

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Figure 1 shows the XPS spectra (C_{1s} , O_{1s} , N_{1s} and P_{2p}) of CLPE and CLPE-g-MPC. In the C_{1s} spectra of both CLPE and CLPE-g-MPC, a strong peak was observed at 285 eV. This peak is attributed to the carbon atoms in the C–C or C–H groups. In the O_{1s} spectrum of CLPE-g-MPC, a significant peak assigned to the C–O group was observed at 532 eV. This peak is mainly ascribed to the MPC units. Even untreated CLPE exhibited a small peak at 532 eV. In this case, the peak is attributed to oxygen atoms and might suggest the contamination and/or oxidation of the CLPE surface. In the N_{1s} and P_{2p} spectra, clear peaks were observed for CLPE-g-MPC only. Peaks at 403 and 134 eV were assigned to the $-N^+(CH_3)_3$ and phosphate groups, respectively; these peaks are characteristic of the phosphorylcholine in the MPC units. Table I summarizes the elemental compositions of the surfaces of untreated CLPE and CLPE-g-MPC. The measured contents of nitrogen (N) and phosphorous (P) in the CLPE-g-MPC was 5.1 and 5.2, respectively. These values were almost equivalent to the theoretical values (N = 5.3, P = 5.3) of MPC polymer.

Figure 2 shows the FT-IR/ATR spectra of CLPE and CLPE-g-MPC. A transmittance absorption peak was observed at 1460 cm^{-1} for both CLPE and CLPE-g-MPC. This peak is attributed mainly to the methylene (CH_2) chain in the CLPE substrate since the peak intensity is very strong and it is unchanged between the CLPE and the CLPE-g-MPC. However, the transmittance absorption peaks at 1240 , 1080 , and 970 cm^{-1} were observed only for the CLPE-g-MPC. These peaks are ascribed to the phosphate (P–O) group in the MPC unit. Similarly, the transmittance absorption peak at 1720 cm^{-1} observed for CLPE-g-MPC only corresponds to the ketone group in the MPC unit.

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3 The relative P–O group index was calculated from the ratio of the FT-IR peak intensities at 1080
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5 and 1460 cm^{-1} as a measure of the amount of MPC unit grafted onto the CLPE surface; this was
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7 done because the peak intensity at 1460 cm^{-1} remains unchanged.
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12 Figure 3 shows the calculated P–O group index as a function of the irradiation time for the
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14 CLPE-*g*-MPC specimens. The P–O group index increased as the irradiation time was increased.
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19 Figure 4 shows the static water-contact angle as a function of the calculated P–O group index for
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21 the CLPE-*g*-MPC specimens. The static water-contact angle on the untreated CLPE was 88° and
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23 decreased markedly with an increase in the P–O group index. When the P–O group index was
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25 greater than 0.3, the static water-contact angle became constant at the low value of 15°.
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31 Figure 5 shows cross-sectional TEM images of CLPE-*g*-MPC produced with various ultraviolet
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33 irradiation times during polymerization. Lamellae of the order of 100 to 400 nm in length and 10
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35 to 20 nm in thickness were observed in the CLPE substrate regardless of irradiation time, and the
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37 lamellae were 50 to 100 nm in length and 5 to 15 nm in thickness near the surface. With irradiation
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39 times longer than 45 min, a grafted MPC polymer layer 100 to 200-nm thick was clearly observed
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41 on the surface of the CLPE substrate. The MPC-covered region was coexistent with uncovered
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43 regions after an irradiation time of 23 min, although the thickness on the MPC polymer layer of the
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45 covered region remained the same (100 to 200 nm). With irradiation for 11 min, no MPC graft
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47 layer was observed on the surface of the CLPE. These results indicate that the density of the
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49 grafted MPC polymer can be controlled by the polymerization time. This is attributable to the fact
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51 that the number of polymer chains produced in a radical polymerization reaction is generally
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2 correlated with the photo-irradiation time.
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6 Figure 6 shows the gravimetric wear of CLPE-g-MPC with various polymerization irradiation
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8 times during the hip joint simulation test. The CLPE-g-MPC cups were found to wear significantly
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10 less than the untreated CLPE cups. The wear of the CLPE-g-MPC cups subjected to 23 min of
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12 irradiation started to increase after 2.5×10^6 cycles. Table II shows the wear rate of the
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14 CLPE-g-MPC cups with various P-O group indexes and irradiation times during the hip joint
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16 simulation test. We defined the initial wear rate as that from the start to 0.5×10^6 cycles, and
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18 considered the steady wear rate as that from 2.5×10^6 to 3.0×10^6 cycles. All of the untreated
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20 CLPE and CLPE-g-MPC cups showed low initial wear rates of -1.42 to -3.74 mg/ 10^6 cycles. The
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22 steady wear rate of the untreated CLPE cups and the CLPE-g-MPC cups with a low P-O group
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24 index of 0.11 increased to 3.68 and 4.64 mg/ 10^6 cycles, respectively. In contrast, the wear rates of
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26 the CLPE-g-MPC cups with high P-O group indexes, i.e., 0.46 and 0.48, were markedly lower at
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28 -1.12 and 0.16 mg/ 10^6 cycles, respectively.
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44 Figure 7 shows the confocal laser scanning microscopy images of the bearing surfaces of the
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46 untreated CLPE and CLPE-g-MPC (irradiation time = 90 min) cups before and after the
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48 melt-recovery test that was performed after the simulator test. Before melt-recovery test, scratches
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50 were seen in the bearing surfaces of the untreated CLPE and CLPE-g-MPC. After melt-recovery
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52 test, these scratches completely disappeared from the bearing surfaces. In addition, clear regular
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54 circular machining marks were observed on the surface of the CLPE-g-MPC, while no marks were
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56 observed on the untreated CLPE, indicating that the former was not significantly worn.
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DISCUSSION

We have developed an artificial hip joint that uses CLPE-g-MPC on the bearing surface; it has been designed to reduce wear and suppress bone resorption. Our previous study reported the effects of graft polymerization of MPC onto the CLPE surface.¹³ The MPC grafting markedly decreased the friction and amount of wear. In the present study, we investigated the structure and properties of the MPC polymer layer formed on the CLPE surface by photo-induced radical graft polymerization; this report discusses the wear-resistant properties of CLPE-g-MPC in terms of the characteristics of the MPC polymer layer.

After 3.0×10^6 cycles of the hip joint simulator test, we confirmed that the CLPE-g-MPC cups with a P–O group index of 0.32 to 0.48 exhibited a relatively low steady wear rate (-1.12 to 0.68 mg/ 10^6 cycles). This indicates that CLPE-g-MPC cups with a P–O group index greater than 0.32 achieve a $> 80\%$ reduction in their steady wear rate compared with untreated CLPE as well as CLPE-g-MPC cups with a low P–O group index (0.11) and low density of grafted MPC polymer chains. Since MPC is a highly hydrophilic compound, poly(MPC) is water-soluble. In fact, as shown in Figure 4, the water-wettability of the CLPE-g-MPC surface was considerable greater than that of an untreated CLPE surface. Therefore, the artificial hip joint bearing with the grafted MPC polymer surface exhibited considerably higher lubricity than that without the MPC polymer. The significant reduction in the coefficient of friction of the grafted MPC polymer¹³ resulted in a substantial improvement in wear resistance. We assumed that the bearing surface of the artificial

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3 hip joint combined with MPC polymer exhibited the fluid film lubrication (or mixed lubrication) of
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6 the intermediate hydrated layer; this suggests that this novel artificial hip joint mimics the natural
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9 joint cartilage.

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12 It is assumed that several important issues are involved in the long-term retention of the benefits
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15 of MPC polymer used in artificial joints under variable and multidirectional loads: strong bonding
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18 between the MPC polymer and the CLPE surface, high mobility of the free end groups of the MPC
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21 polymer, and a high density of the introduced MPC polymer. These considerations are based on
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24 previous studies of charged polymers (polyelectrolytes) reported by Klein, et al.^{26,27} With this in
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27 mind, we selected photo-induced radical graft polymerization to produce C–C covalent bonding
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30 between a carbon atom of CLPE and an end group of the MPC polymer chain. As shown in Figure
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33 5, the crystalline structure of the CLPE substrate is unchanged even after the grafting of MPC,
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36 regardless of irradiation time (polymerization time). This indicates that ultraviolet-induced radical
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39 graft polymerization does not affect the structure of the CLPE substrate. The unchanged structure
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42 of the CLPE substrate itself is very important because the CLPE cup acts not only as a bearing
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45 material but also as a structural material in the artificial hip joint. Furthermore, when the MPC
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48 layer disappears on the substrate surface, the exposed CLPE substrate may have lower wear than
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51 uncross-linked polyethylenes. We therefore deemed that the substrate was CLPE, although it was
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54 shielded by the MPC layer. In a previous study using gamma irradiation,²⁸ the
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57 lower-molecular-weight cross-linked GUR1020 materials had higher mechanical properties (tensile
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60 and impact properties) for all doses compared to the higher-molecular-weight cross-linked

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GUR1050 materials. Nevertheless, the cross-linked GUR1020 materials exhibited the same wear rate as the cross-linked GUR1050 materials. Therefore, we selected the GUR1020 compression-molded bar stock as a CLPE substrate.

In order to obtain an MPC polymer layer with high density, the irradiation time must be controlled.²⁰ The density of the MPC polymer chains on the surface of the CLPE gradually increased with increasing irradiation time and the entire surface of the CLPE was coated using polymerization times longer than 45 min. As shown in Figure 5, with longer irradiation, the thickness of the MPC polymer layer remained the same (100 to 200 nm). In the CLPE-g-MPC cups with a high surface density of MPC graft chains, the MPC graft chains are assumed to stand up to exhibit a brush like structure.^{29, 30} It is generally well-known that the reaction rate of radical polymerization is extremely high.³¹ The molecular weight of grafted polymer is therefore controlled by monomer concentration. When the MPC polymer layer has brush like structure, the layer thickness might depend on the molecular weight of grafted MPC polymer. On the other hand, Figure 4 implies that the density of the MPC polymer chains on the surface of the CLPE was different, even if the water-wettability of the CLPE-g-MPC was constant (as low as 15°); this is because the P–O group index changed remarkably within the range of 0.3 and 0.7.

As mentioned above, the steady wear rate of CLPE-g-MPC cups with a high P–O group index was relatively low even after 3.5×10^6 cycles in the simulator test. As shown in Figure 7, clear machining marks with regular circles remained on the surface of CLPE-g-MPC cups even after the simulator test. In other words, the CLPE-g-MPC cups were virtually unworn, which is consistent

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3 with the relatively low wear observed in the hip joint simulator tests.
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6 Table II shows that several CLPE-g-MPC cups exhibited a slight increase in weight (wear rate
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8 was negative); this was attributable to slightly enhanced fluid absorption over and above the fluid
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10 absorption by the load-soak controls. When using the gravimetric method, we corrected the weight
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12 loss for the fluid absorption by subtracting the weight gain that occurred in the load-soak controls.
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14 Since the wear cups are subjected to motion and load, there are limitations to this correction;
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16 therefore, they are observed to absorb slightly more fluid than their load-soak controls. However,
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18 as a result, the correction for fluid absorption by using the load-soak controls data as the correction
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20 factor leads to a slight underestimation of the actual weight loss.
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31 The excellent functions of CLPE-g-MPC could avoid the activation of cell systems by the wear
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33 particles, thus entirely preventing periprosthetic osteolysis and subsequent aseptic loosening.¹³ In
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35 view of its superior mechanical and biological advantages, the CLPE-g-MPC is widely expected to
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37 be the next-generation bearing material for artificial hip joints. Arrangements are now being made
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39 for the conduction of clinical trials.
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46 In this study, we investigated the surface physical properties of CLPE-g-MPC. After a hip joint
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48 simulator test, we confirmed that CLPE-g-MPC cups with a high surface density of MPC graft
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50 chains exhibited a relatively low and steady wear rate. When compared with cups with untreated
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52 CLPE and those with CLPE-g-MPC with a low P-O group index (cups with low density of grafted
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54 MPC polymer chain), these CLPE-g-MPC cups exhibited an 80% reduction in their steady wear rate.
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60 Thus, it appears that CLPE-g-MPC markedly reduces the generation of wear particles. However,

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the grafting of MPC polymer at a high density is essential to maintain the wear-resistance of CLPE-*g*-MPC as an orthopedic bearing material over long periods of time. We conclude that grafting MPC onto CLPE is a useful method for maintaining efficient lubrication of artificial hip joints over a long period.

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Figure captions

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- TABLE I. Surface elemental compositions (%) of CLPE (untreated) and CLPE-*g*-MPC
- TABLE II. Typical P–O group index and wear rate in hip joint simulator tests
- Figure 1. XPS spectra of CLPE-*g*-MPC. (a) CLPE (untreated), (b) CLPE-*g*-MPC.
- Figure 2. FT-IR/ATR spectra of CLPE-*g*-MPC. (a) CLPE (untreated), (b) CLPE-*g*-MPC.
- Figure 3. P–O group index as a function of irradiation time for CLPE-*g*-MPC.
- Figure 4. Static water-contact angle as a function of P–O group index for CLPE-*g*-MPC.
- Figure 5. Cross-section TEM images of CLPE-*g*-MPC with various photo-polymerization times. Bar = 200 nm. (a) 11 min, (b) 23 min, (c) 45 min, (d) 90 min, and (e) 180 min.
- Figure 6. Weight change of CLPE-*g*-MPC cups with various irradiation times during polymerization in the hip joint simulation test. Bars = Standard deviations.

*P–O group indexes are in parentheses.

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6 Figure 7. Confocal laser scanning microscope images of the bearing surfaces of the cups
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8 before and after a melt-recovery test that was performed after the simulator test.
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12 (a) CLPE before melt-recovery test, (b) CLPE after melt-recovery test, (c)
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15 CLPE-*g*-MPC before melt-recovery test, and (d) CLPE-*g*-MPC after
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18 melt-recovery test. Bar = 400 μm .
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Samples	C	O	N	P
Untreated CLPE	99.6 (100.0) ^a	0.4 (0.0) ^a	0.0 (0.0) ^a	0.0 (0.0) ^a
CLPE- <i>g</i> -MPC	61.8 (57.9) ^a	27.9 (31.6) ^a	5.1 (5.3) ^a	5.2 (5.3) ^a

^aTheoretical elemental compositions of CLPE and MPC polymer are shown in the parentheses, respectively.

TABLE I Surface elemental compositions (%) of CLPE (untreated) and CLPE-*g*-MPC

Irradiation time (min)	P-O group index (I_{1080}/I_{1460})	Initial wear rate (mg/10 ⁶ cycles)	Steady wear rate (mg/10 ⁶ cycles)
0 (untreated CLPE)	0.00	-1.42 (0.78) ^a	3.68 (0.20) ^a
23	0.11	-2.78 (0.76) ^a	4.64 (6.38) ^a
45	0.32	-2.58 (0.08) ^a	0.68 (0.80) ^a
90	0.46	-3.60 (0.48) ^a	-1.12 (0.32) ^a
180	0.48	-3.74 (0.50) ^a	0.16 (0.08) ^a

^aThe standard deviation is in parentheses.

TABLE II Typical P-O group index and wear rate in hip joint simulator tests