Friction

Research Article

Synthesis of nature inspired, phosphorylcholine moieties and poly(ethylene oxide) brushes containing copolymers which synergise steric repulsion and hydration lubrication for articular cartilage

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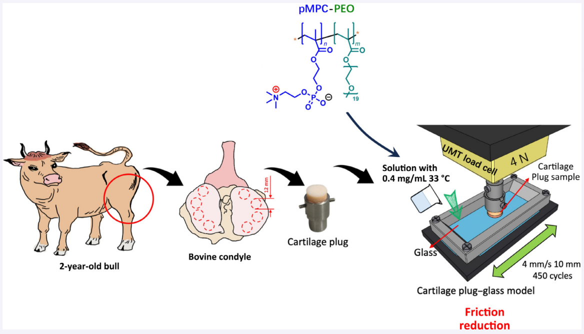

ABSTRACT: Inspired by nature, hydrophilic diblock brush copolymers containing both phosphorylcholine groups and poly(ethylene oxide) (PEO) side chains were synthesized by successive reversible addition-fragmentation chain transfer (RAFT) polymerization of the zwitterionic monomer 2-methacryloyloxyethyl phosphorylcholine (MPC) and the PEO-containing macromonomer poly(ethylene oxide) methyl ether methacrylate (PEOMEMA) for the first time. The lubricating effect of several diblock brush copolymers and one gradient copolymer of MPC and PEOMEMA was evaluated by tribological measurements in polydimethylsiloxane (PDMS)–glass and cartilage–glass systems which were placed in phosphate-buffered saline (PBS) solutions of the polymers. The best lubrication was provided by the diblock copolymer with a relatively long poly(2-methacryloyloxyethyl phosphorylcholine) (pMPC) block and the copolymer of gradient structure. The average dynamic coefficient of friction (COF) in the PDMS–glass system at a copolymer concentration of0.4 mg/mL was only 0.004–0.007, while COF values of the copolymers in the cartilage–glass system after 450 sliding cycles reached 0.06–0.07. The excellent lubrication effect of the diblock and gradient copolymers of MPC and PEOMEMA is attributed to hydration lubrication provided by pMPC synergistically combined with steric repulsion from PEOMEMA. Entrapment of diblock brush copolymers between sliding surfaces was sufficient to provide effective lubrication, thus enhancing the efficacy of the diblock brush copolymers as potential additives for intraarticular injections.

KEYWORDS: phosphorylcholine; poly(ethylene oxide) (PEO); reversible addition-fragmentation chain transfer (RAFT) polymerization; cartilage lubrication; coefficient of friction (COF)

1 Introduction

A healthy human joint exemplifies superlubrication with a very low coefficient of friction (COF) ranging from 0.001 to 0.01, even under routine physiological pressures of 4–10 MPa [1, 2]. Unfortunately, knee osteoarthritis (OA) is a highly spread disorder and a primary contributor to global disability, with a likelihood of further escalation in the forthcoming years [2, 3]. Joint pain due to OA is mainly caused by the degradation of cartilage tissue and the breakdown of its natural lubrication ability. In the early stages of OA, viscosupplementation is often performed for pain relief, which requires multiple intraarticular injections of hyaluronic acid (HA) [4–6]. HA assists in increasing the viscosity of synovial fluid and, in theory, can interact with exposed chondrocytes and the damaged cartilage matrix. Although the efficacy of viscosupplementation is still under debate [7], this treatment gives rise to an excellent delivery route for other biocompatible and bioactive molecules into the joint cavity, enabling further enhancement of lubrication and relief of pain.

Inspired by the diversity of molecular structures in synovial fluid—hyaluronic acid, lubricin, aggrecan, and phospholipids, many new polymers with various architectures have been investigated for lubrication enhancement [8]. Among these alternative materials are synthetic zwitterionic polymers. The most

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extensively studied zwitterionic polymer is poly(2-methacryloyloxyethyl phosphorylcholine) (pMPC), which is well known for its biocompatibility and ability to mimic the aforementioned phospholipids [9, 10]. Due to their unique properties, 2-methacryloyloxyethyl phosphorylcholine (MPC) polymers are suitable for various applications, such as biomedical devices, coatings, and lubricants [11–14].

MPC polymers have typically been used to reduce friction and enhance lubrication in the form of a coating [15–19]. Various types of copolymers containing MPC units have been synthesized and explored, including graft-derivatives of natural polymers (e.g., chitosan [20, 21] or hyaluronic acid [22, 23]) and synthetic polymers (e.g., polydimethylsiloxane (PDMS) [24, 25] or poly(N-isopropylacrylamide) (PNIPAAm) nanospheres [26]), as well as amphiphilic statistical [27–30] and block [30–32] copolymers. The COF of the grafted copolymer PDMS-pMPC was 90% lower than that of pristine PDMS [24]. By increasing the ratio of MPC to poly(vinylmethylsiloxane-co-dimethylsiloxane) in the copolymer, the COF value decreased from 1.4 to 0.01 [29]. The COF was significantly reduced from 0.124 for the neat titanium alloy to 0.051 for the dopamine methacrylamide (DMA)–MPC copolymer-coated surface; moreover, the COF was almost independent of frequencies and pressures [33]. The COF value of the copolymers of MPC and DMA at a loading force of 35 MPa decreased from 0.018 to 0.009 with the increase of the copolymer concentration by 50% [33].

Phosphorylcholine moieties present on polymer molecules constitute a unique structure that imparts excellent lubricating properties by preventing close contact and adhesion between surfaces [13, 34, 35]. The main explanation of the excellent lubricating properties of MPC polymers was developed by Klein's group. [18, 36, 37] which was termed hydration lubrication (one type of boundary lubrication). Basically, two main aspects of hydration lubrication are addressed. First, the strong binding of water molecules to the mantled ionic charges forms a hydration shell around the negative and positive charges (PO^{4-}, $N^{+}(CH_3)_3$) of the phosphorylcholine group (over 15 water molecules per MPC headgroup) [38–41]. Fu et al. [38] and Ishihara et al. [40] proved the formation of an inner salt between the positive trimethylammonium and negative phosphate groups in aqueous solutions, and the arrangement of water molecules into a "clathrate" structure around the trimethylammonium group. The bound water around the phosphoryl choline group is also known as non-freezing water. Namely, it is not able to crystallize due to robust molecular interactions with the matrix polymer. The second aspect of the hydration lubrication mechanism is related to the rapid relaxation of hydration layers [37, 42]. This property enables the material to exhibit fluid-like behaviour when sheared at rates lower than the relaxation rates [41]. Thus, the hydrated shells of MPC are highly fluid, serving as effective lubricating layers.

Another polymers widely used for reduction of friction in aqueous solutions are those containing poly(ethylene oxide) (PEO) segments. PEO, alternatively referred to as poly(ethylene glycol) (PEG), is a water-soluble polymer extensively examined for both its aqueous solution properties [43, 44] and interfacial properties [45–47]. Müller et al. [48] have demonstrated that poly(L-lysine) containing poly(ethylene glycol) grafts adsorbs onto the silica surface due to electrostatic interactions and forms dense brush layers that provide good lubrication. The low friction between polymer-coated surfaces is attributed to steric repulsion—another type of boundary lubrication, defined as the lubrication of surfaces by molecules that hold on to a thin layer of water (e.g., the lamina splendens of the articular cartilage surface) [19, 49, 50]. Pettersson et al. [51] demonstrated that bottle-brush polymethacrylate-type copolymers with randomly distributed PEO side chains and a positively charged backbone in aqueous media were firmly attached to the surfaces, creating a highly hydrated PEO layer and providing extremely low friction between coated surfaces. The lowest COF (0.006) was observed for the copolymer with a low charge density and a high density of PEO chains, confirming the strong contribution of the extended conformation of the adsorbed layer [52]. The excellent lubricity was explained by several factors, such as low interpenetration of the opposing brushes, high fluidity of the hydration layers, and differences in osmotic pressure between the brush layer and the surrounding medium [53]. Thus, for excellent lubrication, the polymer layers on a surface should be dense, stretched to prevent interpenetration between opposing layers, and sufficiently hydrated to form a fluidic interface.

Statistical copolymers of MPC with styrene and various alkyl methacrylates were synthesized by conventional free-radical copolymerization [28, 54, 55]. Later, various methods of reversible deactivation (living) radical polymerization were employed, which enabled to synthesize MPC copolymers with more complex architectures, such as block-type and graft-type copolymers [32, 56–59]. Recently, superhydrophilic gradient-like brush copolymers containing MPC units and PEO side chains were successfully synthesized by reversible addition-fragmentation chain transfer (RAFT) copolymerization [59].

In the present study, we aimed to prepare the brush-type copolymers carrying both phosphorylcholine groups and PEO side chains, and to evaluate the effect of these two types of functionalities present on the same backbone on the biolubrication behaviour in aqueous solutions as a potential application for viscosupplementation improvement. To the best of our knowledge, there are no published papers on the synthesis and application of diblock copolymers of MPC and poly(ethylene oxide) methyl ether methacrylate (PEOMEMA). We expect that the block structure of such copolymers will be beneficial for exploring several mechanisms of articular cartilage lubrication which can complement each other. An intermediate but important task was the synthesis of the diblock copolymers via successive RAFT polymerization of the zwitterionic monomer MPC and PEO-containing macromonomer PEOMEMA. The synergetic effect of PEO brushes and phosphoryl choline moieties of the copolymers on the lubricating efficiency of articular cartilage is pointed out and discussed.

2 Materials and methods

A description of the materials used, as well as the methods of polymer synthesis and characterization, is presented in the Electronic Supplementary Material (ESM).

2.1 Evaluation of lubrication

2.1.1 Preparation of PDMS probe

Hemispherical PDMS probes were utilized in preliminary experiments to figure out the influence of MPC–PEOMEMA copolymer concentration in tribological tests. The PDMS mixed solution (monomer/cure agent 10:1 v/v, Sylgard-184, Dow Corning, USA) was added in a 96-well clear polystyrene (PS) microplate (Greiner Bio-One, Germany). The plate was placed in a vacuum chamber at 80 °C overnight (> 12 h). After curing, the probes were then removed out from the 96-well microplate gently. The PDMS probe had a radius of 3.1 mm and a length of 10 mm, the same size as that of a single well of the 96-well microplate. n-hexane (Sigma-Aldrich, USA) was applied to remove dust attached on the PDMS surface. Then, PDMS probe was washed by Milli-Q water through sonication for 15 min. The detail was referred to our previous work [60].

2.1.2 *PDMS–glass tribological experiment*

The tribological experiment was carried out using UMT-3 universal mechanical tester (Bruker Corporation, USA) in a pin-on-plate reciprocating sliding model. The PDMS cylinder was fixed under the UMT load cell (DFM-1.0, Bruker, USA) and rubbed against a borosilicate glass (Schott BK-7, Gerhard Menzel GmbH, Germany) (Fig. 1). A distance of ±12 mm, a vertical load of 4 N, and a sliding speed of 4 mm/s were chosen to simulate the swing phase of human gait cycle [61]. 220 reciprocate cycles were applied (back and forward) for 1,320 s. For figuring out the influence of MPC–PEOMEMA copolymer concentration in tribology, various MPC–PEOMEMA copolymer solutions (2 mg/mL in 10 mM PBS buffer) were prepared in advance. During the measurement, 2 mL of PBS buffer was initially added to the glass surface, and 50 μL of the copolymer solution was dosed every 20 cycles interval until 220 cycles, resulting in the concentration of MPC–PEOMEMA copolymers between PDMS and glass be 0 (cycle 1–20), 0.048 mg/mL (cycle 21–40), 0.096 mg/mL (cycle 41–60), and up to 0.400 mg/mL (cycle 201–220). For comparison, pure PBS buffer was used as the lubricant throughout the rubbing test as a control. The whole rubbing experiment was kept at a constant temperature of 33 °C, which meets the intra-articular temperature in the knee joint during mild activity [62]. The average dynamic COF for every 20 cycles was measured corresponding to different concentrations of MPC–PEOMEMA copolymer solution.

2.1.3 *Preparation of osteochondral plug*

Fresh bovine knee joints were harvested from two-year-old bulls at an abattoir (Kroon Vlees b.v., the Netherlands) and dissected 24 h after slaughter. The femoral condyles of bovine knee joint were chosen for cutting and drilling cartilage plugs (diameter 12 mm). Whole preparation was performed at room temperature (20–24 °C). The cartilage surface was kept wet and cool using PBS buffer during the drilling and cutting. Osteochondral plugs were obtained after drilling through a stainless-steel cylinder (inner diameter 12 mm). Before further tribological measurements, the cartilage plugs were stored in PBS buffer at 4 °C and used within 24 h. The morphology and topography of the cartilage surface were well characterized, with more details available in latest publications [7, 61, 63]. The roughness measured by atomic force microscopy (AFM) was found to be 496±67 nm [61].

2.1.4 *Cartilage–glass tribology test*

Frictional experiments were performed on a cartilage–borosilicate glass model which was immersed in a copolymer solution with a

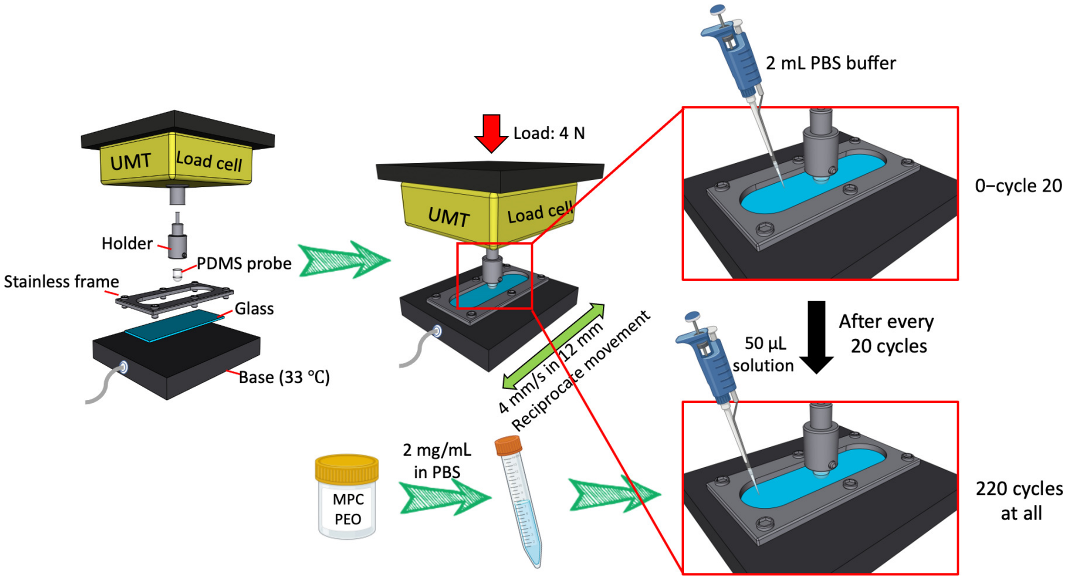


Fig. 1 Schematic representation of the basic setup for PDMS–glass tribology measurement.

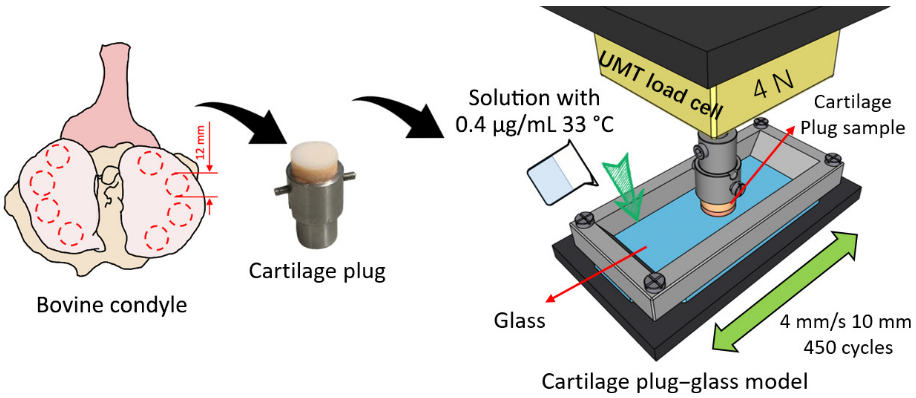


Fig. 2 Schematic representation of basic setup for cartilage plug–glass tribology measurement.

concentration of 0.4 mg/mL, using UMT-3 with reciprocal sliding motion (±10 mm at 4 mm/s under a load of 4 N). A 4 N load results in a contact pressure of 0.4 MPa [64]. Each measurement lasted 450 cycles (1 h) at 33 °C. The average dynamic COF for each cycle was measured. To further simplify the display, the mean COF value of every 50th cycle was picked up up to 450 cycles (i.e., cycle 0, cycle 50, cycle 100, until cycle 450).

3 Results and discussion

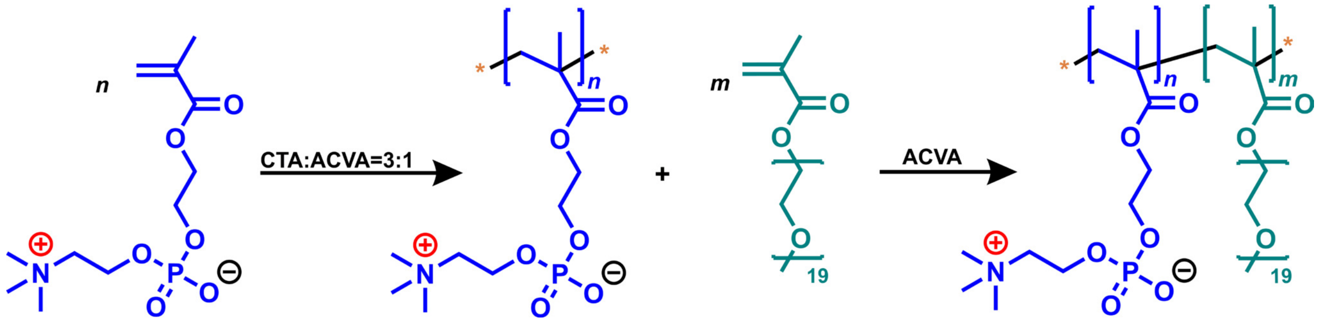
3.1 Synthesis and characterization of the diblock copolymers of MPC and PEOMEMA

Successive RAFT polymerization of MPC and $PEO_{19}MEMA$ to yield the diblock copolymer pMPC-b-p($PEO_{19}MEMA$) is presented in Scheme 1. RAFT polymerization was carried out in a 3:1 (v/v) methanol/water mixed solvent, using 4,4′ -azobis-(4-cianovaleric acid) (ACVA) as an initiator and 4-(((butylthio)carbonothioyl)thio)-4-cyanopentanoic acid (CTA) as the RAFT chain transfer agent. The structural formulas of ACVA and CTA are presented in the ESM.

The polymerization of MPC in the mixed methanol (MeOH)/water (3:1, v/v) solvent was studied in our previous publication [65]. Using the same procedure, we prepared three samples of pMPC with different chain lengths (degree of polymerization (DP) 18, 27, and 41) and used them as macro-CTAs for chain extension with PEOMEMA units, in which the polymerisation degree of ethylene oxide was 19 or 9 (i.e., $PEO_{19}MEMA$ or $PEO_{9}MEMA$, respectively). The number-average molecular weight (M_n) of these pMPC samples, determined by size exclusion chromatography (SEC), was 10, 15.5, and 23.3 kDa, respectively; the dispersity index $Đ$ of the polymers was 1.09, 1.08, and 1.10, respectively. Chain extension (formation of the second block composed by PEOMEMA units) was followed by recording SEC elution curves of the reaction mixtures.

SEC elution curves of the reaction mixtures after RAFT polymerization of MPC and chain extension of pMPC with the chains of $PEO_{9}MEMA$ or $PEO_{19}MEMA$ are shown in Fig. 3. All elution curves contain two peaks: a polymer peak at lower retention volume and a residual monomer peak at higher retention volume. It means that the monomer conversion at the moment of sampling was not very high. Residual monomer was successfully removed from pMPC by reprecipitation from methanol, and the purified and dried pMPC was used for the chain extension. During chain extension, the peak associated with residual monomer PEOMEMA was usually larger, indicating lower conversion of PEOMEMA. Nevertheless, the peaks on elution curves attributed to the block copolymer appeared unimodal and shifted towards lower retention volumes relative to the pMPC peak (Fig. 3). This proves the formation of block copolymers with molecular weights considerably higher than those of pMPC. The peaks on SEC elution curves of the reaction mixture attributed to pMPC and the block copolymers partially overlap (Fig. 3), which raises a question about possible contamination of the block copolymers with homopolymer molecules. In order to dispel any doubts, SEC elution curves of the diblock copolymers after purification by dialysis through a 12–14 kDa molecular weight cut-off (MWCO) membrane were recorded (Fig. S6 in the ESM). These curves are unimodal and symmetrical, indicating that the diblock copolymers are uncontaminated and exhibit low dispersity. The formation of diblock copolymers was further confirmed by diffusion-ordered spectroscopy (DOSY) spectra of the copolymers, which indicated no evidence of homopolymers (Figs. S8–S10 in the ESM). The diffusion rates of $pMPC_{41}$, $pMPC_{41}$-b-p($PEO_{19}MEMA$)$_{12}$, and $pMPC_{41}$-b-p($PEO_{9}MEMA$)$_{17}$, calculated using DOSY spectra alongside stacked diffusion spectra, were 3.25×10^{-6}, 1.95×10^{-6}, and 1.93×10^{-6} cm^2/s, respectively. Obviously, the diffusion rates of the diblock copolymers are significantly lower than those of pMPC used as the macro-CTA for chain extension with PEOMEMA units. The similarity of the diffusion rates of both diblock copolymers is in accordance with nearly identical molecular weights of the copolymers. Thus, diffusion rates provide strong evidence that polymers with larger molecular weights were synthesized during the chain extension of pMPC chains with PEOMEMA. The dispersity $Đ$ of the diblock copolymers is not low but reasonable, about 1.3–1.6 (Table 1), which is a typical value for diblock copolymers synthesized by RAFT polymerisation.

^1H nuclear magnetic resonance (NMR) spectra of the polymers are presented in Fig. 4. Characteristic chemical shifts of pMPC in MeOD-d4 appear at 4.35, 4.25, 4.10, 3.72, and 3.33 ppm, which are attributed to the protons in $–O–CH_2–CH_2–O–P–$, $P–O–CH_2–CH_2–N–$, $–O–CH_2–CH_2–O–P–$, $–P–O–CH_2–CH_2–N–$, and $–N(CH_3)_3$ groups, respectively (curve 1 in Fig. 4). Characteristic chemical shifts of p($PEO_{19}MEMA$) in MeOD-d4 are at 4.14, 3.66, and 3.37 ppm, which are attributed to protons in $–COO–CH_2–CH_2–O–$, $–(–O–CH_2–CH_2–O–)_x–$, and $–O–CH_3$ groups, respectively (curves 3 and 4 in Fig. 4). In the diblock copolymers spectra, some chemical shifts, attributed to different monomeric units, appear in close vicinity and partially overlap (curves 2 and 3 in Fig. 4). The copolymer composition was calculated using the chemical shifts at 3.33 and 3.37 ppm, which belong to MPC and PEOMEMA, respectively (inset in Fig. 4). The composition of the diblock copolymers calculated from ^1H NMR spectra is presented in Table 1. Calculation of the length (DP) of pPEOMEMA block was based on SEC data of the diblock copolymers and pMPC, also on copolymer compositions determined by ^1H NMR spectroscopy, and DP of the first block determined by SEC. The DP of the second block (pPEOMEMA)



Scheme 1 Synthesis of diblock copolymers pMPC-b-p($PEO_{19}MEMA$).

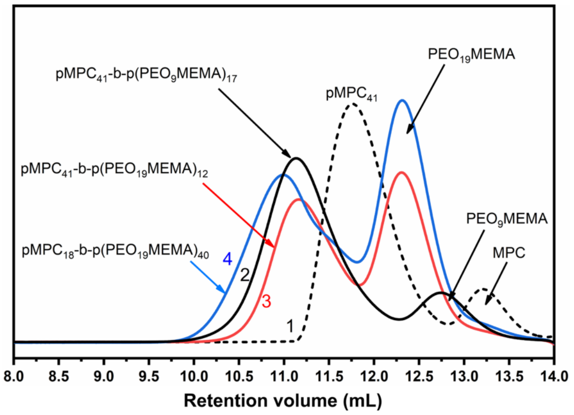


Fig. 3 SEC elution curves of the reaction mixtures taken after 8 h of RAFT polymerization of (1) MPC and 24 h of chain extension of pMPC with (2) PEO$_9$MEMA and (3, 4) PEO$_{19}$MEMA.

calculated by these two methods was similar with slightly higher values obtained by NMR. The DP of the second block was not large, ranging from 20 to 40 (Table 1). The DP values lower than expected were predetermined by the relatively low conversion (60–70 mol%) of PEO$_{19}$MEMA during the chain extension. This observation is consistent with Ref. [66], which discloses obstacled chain extension by PEO$_{19}$MEMA units with long PEO chains.

The (co)polymers delivered for tribology tests are presented in Table 2. The set of polymers includes homopolymers pMPC$_{41}$ and p(PEO$_{19}$MEMA)$_{62}$, two block copolymers containing the p(PEO$_{19}$MEMA) block—one with relatively long pMPC block pMPC$_{41}$-b-p(PEO$_{19}$MEMA)$_{12}$ and another with relatively short pMPC block pMPC$_{18}$-b-p(PEO$_{19}$MEMA)$_{40}$, block copolymer pMPC$_{41}$-b-p(PEO$_9$MEMA)$_{17}$ with relatively long pMPC block, and gradient copolymer p(MPC-grad-PEO$_{19}$MEMA)$_{69}$. Synthesis and characterization of the gradient copolymer are described in our previous publication [59] and in the ESM as well.

3.2 Lubricating effect of the copolymers of MPC and PEOMEMA

To determine the proper concentration of MPC and PEOMEMA copolymers for articular cartilage lubrication, the PDMS–glass tribological tests were performed before cartilage plug–glass tribological measurements. Figure 5 presents the results from PDMS–glass system placed in PBS solutions containing copolymers of MPC and PEOMEMA.

Figure 5(a) shows the dependence of the dynamic COF on the concentration of various MPC–PEOMEMA copolymers, and Fig. 5(b) compares COF values obtained at a copolymer concentration of 0.4 mg/mL. All solutions except pure PBS (control) showed reduced COF when the concentration increased to 0.4 mg/mL. PBS failed to lubricate the PDMS and glass interface, which was consistent with the results from previous work [67–69]; the COF of the PBS solution was rather stable at around 0.413±0.067 (Fig. 5(b)). The best lubrication was provided by the gradient copolymer p(MPC-grad-PEO$_{19}$MEMA)$_{69}$; the COF at copolymer concentration of 0.4 mg/mL was lowered by 90% to 0.004±0.002. A slightly higher value of COF (0.007±0.002) was observed for the diblock copolymer with a relatively long pMPC block, pMPC$_{41}$-b-(PEO$_{19}$MEMA)$_{12}$. The lubricating effect of the diblock copolymer with a relatively short pMPC block, pMPC$_{18}$-b-(PEO$_{19}$MEMA)$_{40}$, was significantly lower, evidenced by its much higher value of COF (0.088±0.125). Length of PEO chain had little effect on the lubricating properties of the copolymers: replacement of the diblock copolymer pMPC$_{41}$-b-(PEO$_{19}$MEMA)$_{12}$ with a diblock copolymer of similar structure but with a shorter PEO chain, pMPC$_{41}$-b-(PEO$_9$MEMA)$_{17}$, led to COF value increasing from 0.007±0.002 to 0.010±0.006. Thus, all tested copolymers of MPC and PEOMEMA possessed good anti-friction properties, but the best lubrication was provided by copolymers containing a large amount of MPC units. At copolymer concentrations higher than 0.4 mg/mL, the decrease in COP was slow and negligible. We chose 0.4 mg/mL as the optimal copolymer concentration for the following osteochondral plug lubricating measurements.

Figure 6 presents the results of dynamic COF at the cartilage plug–glass interface. The COF for all the samples showed an increasing trend over time (Fig. 6(a)), especially for the control (PBS). This is in accordance with the interstitial fluid pressurization and weeping (IFPW) mechanism of cartilage [7, 70, 71], the experimental proof of which was provided by Caligaris and Ateshian [72] in the form of Eq. (1):

$$\frac{\mu_{\text{eff}}}{\mu_{\text{eq}}} = 1 - (1-\varphi)\frac{W^{\text{p}}}{W} \tag{1}$$

where φ represents the solid fraction of the contact area; $1-\varphi$ is the water content of cartilage at the articular surface, which is around 0.91 for a normal bovine cartilage [73]; W^{p}/W is defined as the interstitial fluid load support; μ_{eff} and μ_{eq} are the time-dependent and equilibrium COFs, respectively. At the start of contact, the cartilage is compressed, causing the release of interstitial fluid in the sliding interface. At this stage, all the load is supported by the fluid, resulting in low COF values. However, as time passes, more fluid is squeezed out from the interface between cartilage and glass, and increasing load is carried by solid-solid contact, leading to an increased COF. In the presence of PBS (control), the COF after 450 cycles was observed to be 0.480±0.048.

pMPC, pPEOMEMA, and the copolymers used in this study

Table 1 Characteristics of the diblock copolymers of MPC and PEOMEMA. *Đ* is dispersity index of a (co)polymer and DP is degree of polymerization in corresponding block

Diblock copolymer	[PEOMEMA]/[CTA]	Composition, MPC (mol%)	M_n (kDa)	*Đ*	DP1, first block	DP2, second block, SEC	DP2, second block, NMR
pMPC-b-p(PEO$_{19}$MEMA)	100	34.6	64.0	1.55	27	51	56
	60	31.0	47.6	1.57	18	40	43
	50	51.9	39.3	1.53	27	25	23
	40	54.0	36.9	1.41	27	23	26
	20	77.4	31.8	1.33	41	12	14
pMPC-b-p(PEO$_9$MEMA)	60	12.2	75.1	1.43	18	72	67
	40	40.9	34.8	1.53	27	39	43
	20	70.7	31.5	1.38	41	17	25

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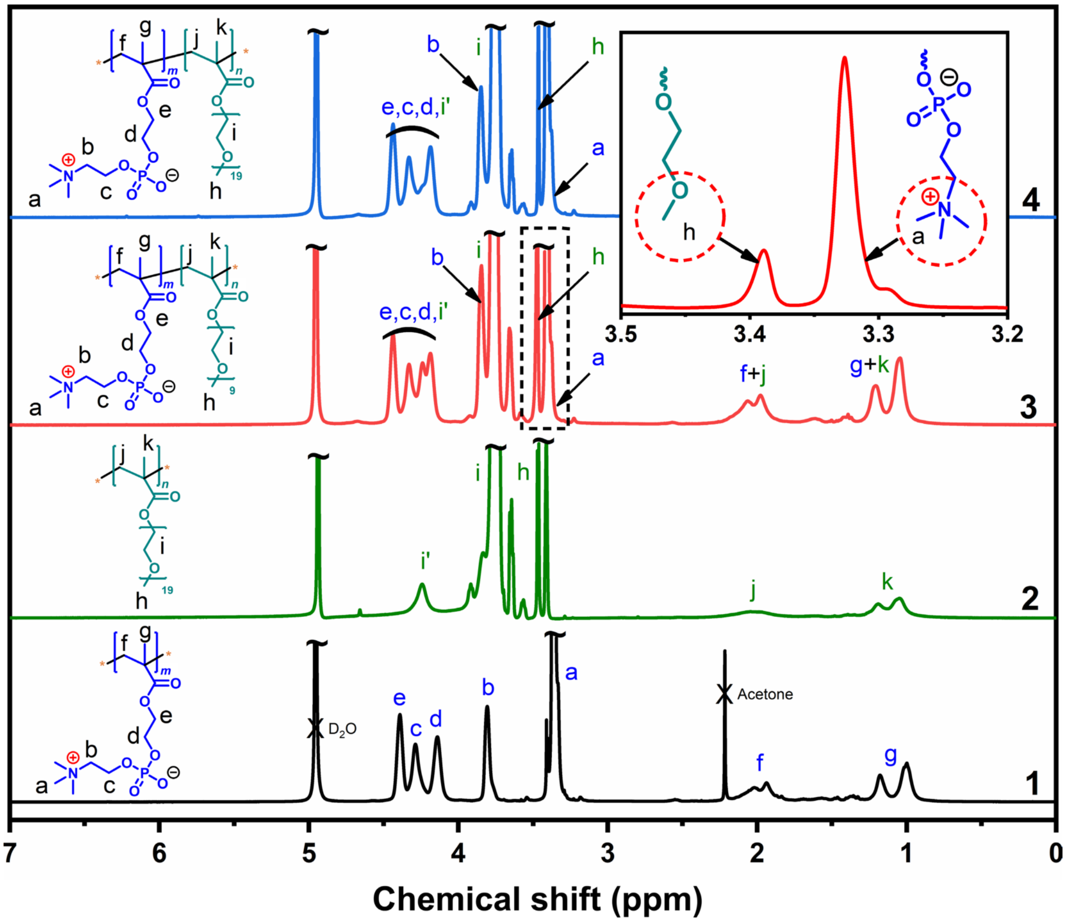


Fig. 4 ^{1}H NMR spectra of pMPC$_{41}$ (1), p(PEO$_{19}$MEMA)$_{62}$ (2), pMPC$_{41}$-b-p(PEO$_9$MEMA)$_{17}$ (3), and pMPC$_{41}$-b-p(PEO$_{19}$MEMA)$_{12}$ in MeOD-d4 (4). Inset top right—expanded region of pMPC$_{41}$-b-p(PEO$_9$MEMA)$_{17}$ spectrum at 3.2–3.5 ppm.

Table 2 Characteristics of the (co)polymers of MPC and PEOMEMA used in tribology tests. *Đ* is dispersity index of a (co)polymer and DP is degree of polymerization in corresponding block

(Co)polymer	Copolymer composition, MPC (mol%)	M_n from SEC (kDa)	*Đ*	DP
pMPC$_{41}$	100	23.3	1.10	41
p(PEO$_{19}$MEMA)$_{62}$	0	59.1	1.37	62
pMPC$_{41}$-b-p(PEO$_{19}$MEMA)$_{12}$	77.4	31.8	1.33	41+12
pMPC$_{18}$-b-p(PEO$_{19}$MEMA)$_{40}$	31.0	47.6	1.57	18+40
pMPC$_{41}$-b-p(PEO$_9$MEMA)$_{17}$	70.7	31.5	1.38	41+17
p(MPC-grad-PEO$_{19}$MEMA)$_{69}$	59.8	49.9	1.41	69

are expected neither to interfere with the fluid pressurization in the cartilage nor with the weeping of the fluid from the cartilage. Since all of these are surface-active molecules, we can expect them to show an effect when there is substantial solid–solid contact between cartilage and glass, i.e., in the later period of sliding. The COF values of pMPC$_{41}$ and p(PEO$_{19}$MEMA)$_{62}$ after 450 cycles were 0.251±0.103 and 0.274±0.014, respectively, which are almost half as compared to the control situation (PBS). The rather high COF value of p(PEO$_{19}$MEMA)$_{62}$ is in accord with previous observations [37] that neutral brushes of poly(ethylene oxide) in aqueous media provide rather weak lubrication. pMPC attached to surfaces usually provides excellent lubrication (is characterized by very low COF value) [42]. On the other hand, pMPC homopolymer, dissolved in water and in aqueous PBS or NaCl solutions, even at high polymer concentrations, demonstrates satisfactory but not particularly good lubrication [74].

Exclusively good lubrication of cartilage was provided by the copolymers p(MPC-grad-PEO$_{19}$MEMA)$_{69}$ and pMPC$_{41}$-b-p(PEO$_{19}$MEMA)$_{12}$; no increase in COF was observed after 450 cycles as the COF at the end increased only to 0.072±0.007 and 0.057±0.021, respectively. These values were 85% and 88% lower than that in the control test (PBS, 0.480±0.048). Thus, a clear synergistic lubrication effect of MPC and PEO segments in the copolymers is demonstrated.

The best lubrication, both between PDMS–glass and cartilage–glass, was provided by the diblock copolymer pMPC$_{41}$-b-p(PEO$_{19}$MEMA)$_{12}$ and gradient copolymer p(MPC-grad-PEO$_{19}$MEMA)$_{69}$. Both copolymers are rich in MPC units and contain long PEO side chains. One should note that the copolymer p(MPC-grad-PEO$_{19}$MEMA)$_{69}$ possesses a strongly expressed gradient microstructure [59], which means that at one end, polymer molecules are rich in MPC units and at the other end in PEO$_{19}$MEMA units. In other words, the microstructure of the copolymer p(MPC-grad-PEO$_{19}$MEMA)$_{69}$ somewhat

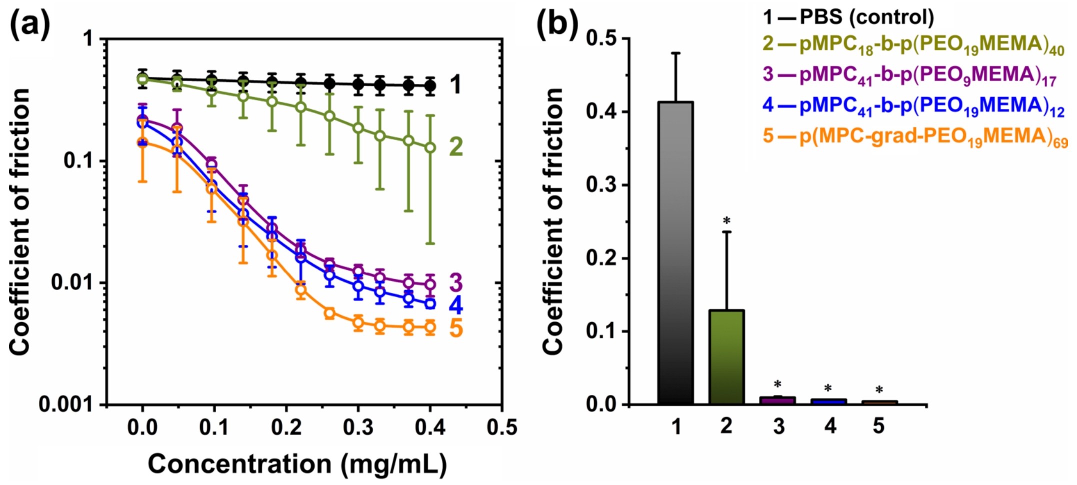


Fig. 5 Dynamic COF of PDMS–glass in PBS solutions of MPC and PEOMEMA copolymers. (a) COF as a function of copolymer concentration; (b) COF at a copolymer concentration of 0.4 mg/mL in PBS solution. The error bars show the standard deviation ($n = 3$); $^*p < 0.5$ compared with control group.

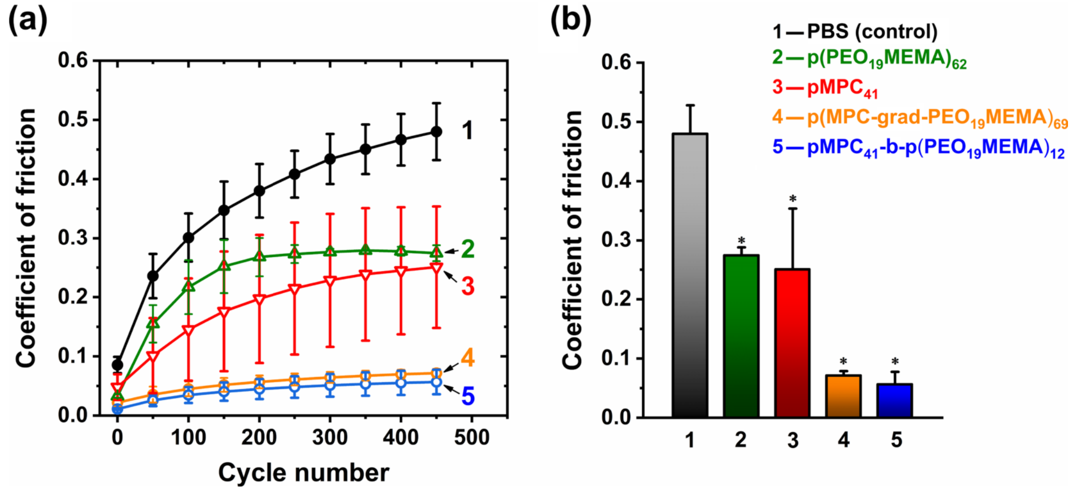
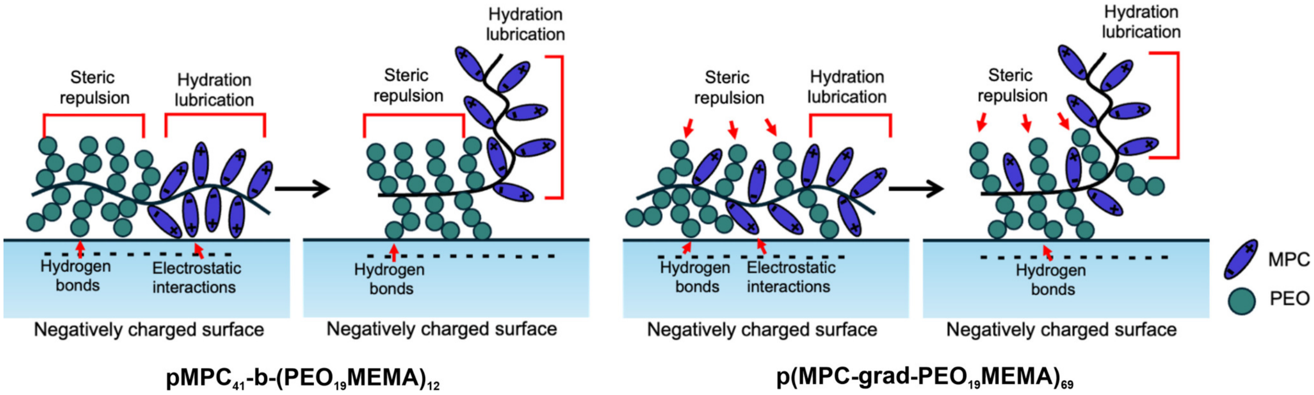


Fig. 6 Dynamic COF of cartilage–glass in PBS solutions of pMPC$_{41}$, p(PEO$_{19}$MEMA)$_{62}$, and copolymers pMPC$_{41}$-b-p(PEO$_{19}$MEMA)$_{12}$ and p(MPC-grad-PEO$_{19}$MEMA)$_{69}$ at a concentration of 0.4 mg/mL: (a) COF as a function of cycle number; (b) COF at cycle number 450. The error bars show the standard deviation ($n = 3$); $^*p < 0.5$ compared with control group.

resembles that of the diblock copolymer pMPC$_{41}$-b-p(PEO$_{19}$MEMA)$_{12}$. We suppose the exclusively good lubricating behaviour of these two copolymers depends on several factors, including a sufficient amount of MPC units and similar macromolecules microstructures.

Trying to answer the question why the lubricating effect of the diblock and gradient copolymers of MPC and PEO$_{19}$MEMA is significantly larger compared to that of the corresponding homopolymers pMPC and p(PEO$_{19}$MEMA), we should refer to the lubrication mechanisms of these polymers and their possibilities to adsorb on contacting surfaces. Excellent lubricating properties of MPC polymers are explained by hydration lubrication, according to which water molecules within hydration shells surrounding zwitterionic groups are firmly attached but remain highly fluid, thus serving as efficient lubricating layers [37]. It is important to note that excellent lubrication is provided by pMPC brushes [16, 42], rather than pMPC homopolymer [74]. pMPC molecules are neutral (phosphate and ammonium groups form an inner salt [40]) and likely have low affinity to the negatively charged glass surface. Such assumption is based on recent findings that internal phosphoryl groups of pMPC are partially (ca. 10%) protonated [75]. Lubrication by PEOMEMA brush polymers arises from the steric repulsive forces between polymer chains and water molecules, which maintain a thin lubricating fluid layer at the interfacial region between sliding surfaces [48]. It is known that pPEOMEMA homopolymer can interact with the silica surface through side chain segments that form hydrogen bonds [76]. The stronger adsorption of the bottle-brush polymer compared to PEO homopolymer is attributed to its higher surface affinity and smaller loss of conformational entropy during adsorption.

Although the question still remains as to why diblock and gradient copolymers of MPC and PEO$_{19}$MEMA perform better than the corresponding homopolymers pMPC and p(PEO$_{19}$MEMA). Based on information presented above, we hypothesise that p(PEO$_{19}$MEMA) blocks help orient and order pMPC blocks through mild interaction with the surface (Scheme 2), and more ordered pMPC blocks resemble polymer brushes. Likely, diblock copolymers initially adsorb preferentially parallel to the surface, with both the pMPC block and the bottle-brush p(PEO$_{19}$MEMA) block in contact with the surface. However, as adsorption proceeds, because of the higher surface affinity, PEO$_{19}$MEMA segments replace MPC segments at the surface (Scheme 2), resulting in a transformation of ordered layer structure. During this transformation, PEO chains accumulate at the surface, and pMPC chains extend away from the surface.



Scheme 2 An illustration showing evolution of interaction between diblock and gradient copolymers of MPC and PEO$_{19}$MEMA with negatively charged surfaces at an initial low surface density (left) and a final high surface density (right) of copolymers.

Thus, it is expected that brush-like layers of pMPC are formed on surfaces, providing hydration lubrication. Furthermore, a water layer between pMPC block and p(PEO$_{19}$MEMA) block (from different macromolecules) is possibly thicker than that between two pMPC blocks or two p(PEO$_{19}$MEMA) blocks, which enhances the lubricating effect.

A conceptual illustration explaining the mechanism of lubrication by diblock and gradient copolymers of MPC and PEO$_{19}$MEMA is presented in Scheme 2.

The boundary lubrication of healthy cartilage is presently attributed to either steric repulsion provided by proteoglycan 4 (PRG4) (lubricin) or hydration lubrication provided by the phosphorylcholine groups of surface-active phospholipids (SAPL). Both molecules adsorb on the cartilage surface in the form of lamina splendens [33, 77–79]. Our results indicate that synergistic interactions between PRG4 and SAPL molecules may be necessary to provide excellent boundary lubrication of healthy cartilage *in vivo*.

4 Conclusions

Hydrophilic diblock brush copolymers containing both phosphorylcholine groups and PEO side chains were synthesized by successive RAFT polymerization of the zwitterionic monomer MPC and PEO-containing macromonomer PEOMEMA. The dispersity of the first block of pMPC was very low ($Đ \leqslant 1.1$), while the dispersity of the diblock copolymers was moderate, typically 1.3–1.6. The degree of polymerization of the second block was controllable and varied between 10 and 70.

The lubricating effect of several diblock copolymers and one gradient copolymer of MPC and PEOMEMA was evaluated by tribological measurements in PDMS–glass and cartilage–glass systems placed in PBS solutions of the polymers. All tested copolymers of MPC and PEOMEMA possessed good anti-friction properties, with the best lubrication provided by the diblock copolymer with a relatively long pMPC block and the copolymer of gradient structure. The average dynamic COF in the PDMS–glass system at a gradient copolymer concentration of 0.4 mg/mL was only 0.004±0.002, while that of the diblock copolymer at the same concentration was 0.007±0.002. The COF values of these copolymers in the cartilage–glass system after 450 cycles of sliding motion were 0.072±0.007 and 0.057±0.021, respectively, which is much lower than those of the corresponding homopolymers pMPC and p(PEO$_{19}$MEMA). The significantly larger lubricating effect of the diblock and gradient copolymers of MPC and PEOMEMA compared to the homopolymers is attributed to higher surface affinity of PEOMEMA segments, which promotes preferential surface interaction and forms brush-like layers of pMPC that provide hydration lubrication.

CRediT authorship contribution statement

Ke Ren: methodology, investigation, data curation, validation, formal analysis, writing–original draft. Marijus Jurkūnas: investigation, data curation, visualization, writing–original draft. Vaidas Klimkevičius: methodology, investigation, data curation. Ričardas Makuška: supervision, conceptualization, validation, writing–review & editing. Prashant K. Sharma: supervision, conceptualization, validation, methodology, writing–review & editing.

Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

Data availability

Data will be made available on request.

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Electronic Supplementary Material

Supplementary material (description of the used raw materials, methods of polymer synthesis and characterization) is available in the online version of this article at https://doi.org/10.26599/FRICT.2025.9441095.

References

[1] Katta J, Jin Z, Ingham E, Fisher J. Effect of nominal stress on the long term friction, deformation and wear of native and glycosaminoglycan deficient articular cartilage. *Osteoarthr Cartil* **17**(5): 662–668 (2009)

[2] Liew J W, King L K, Mahmoudian A, Wang Q K, Atkinson H F, Flynn D B, Appleton C T, Englund M, Haugen I K, Lohmander L S, et al. A scoping review of how early-stage knee osteoarthritis has been defined. *Osteoarthr Cartil* **31**(9): 1234–1241 (2023)

[3] Vos T, Lim S S, Abbafati C, Abbas K M, Abbasi M, Abbasifard M, Abbasi-Kangevari M, Abbastabar H, Abd-Allah F, Abdelalim A, et al. Global burden of 369 diseases and injuries in 204 countries and territories, 1990–2019: A systematic analysis for the Global Burden of Disease Study 2019. *Lancet* **396**(10258): 1204–1222 (2020)

[4] Sato H, Takahashi T, Ide H, Fukushima T, Tabata M, Sekine F,

Kobayashi K, Negishi M, Niwa Y. Antioxidant activity of synovial fluid, hyaluronic acid, and two subcomponents of hyaluronic acid. Synovial fluid scavenging effect is enhanced in rheumatoid arthritis patients. *Arthritis Rheum* **31**(1): 63–71 (1988)

[5] Evanich J D, Evanich C J, Wright M B, Rydlewicz J A. Efficacy of intraarticular hyaluronic acid injections in knee osteoarthritis. *Clin Orthop Relat Res* (390): 173–181 (2001)

[6] Lo G H, LaValley M, McAlindon T, Felson D T. Intra-articular hyaluronic acid in treatment of knee osteoarthritis. *Jama* **290**(23): 3115 (2003)

[7] Wan H P, Ren K, Kaper H J, Sharma P K. A bioinspired mucoadhesive restores lubrication of degraded cartilage through reestablishment of lamina splendens. *Colloid Surface B* **193**: 110977 (2020)

[8] Lin W F, Klein J. Hydration lubrication in biomedical applications: From cartilage to hydrogels. *Acc Mater Res* **3**(2): 213–223 (2022)

[9] Goda T, Miyahara Y, Ishihara K. Phospholipid-mimicking cell-penetrating polymers: Principles and applications. *J Mater Chem B* **8**(34): 7633–7641 (2020)

[10] Moro T, Takatori Y, Kyomoto M, Ishihara K, Saiga K, Nakamura K, Kawaguchi H. Surface grafting of biocompatible phospholipid polymer MPC provides wear resistance of tibial polyethylene insert in artificial knee joints. *Osteoarthr Cartil* **18**(9): 1174–1182 (2010)

[11] Liu G Q, Feng Y, Zhao N, Chen Z, Shi J Q, Zhou F. Polymer-based lubricating materials for functional hydration lubrication. *Chem Eng J* **429**: 132324 (2022)

[12] Lewis A L. Phosphorylcholine-based polymers and their use in the prevention of biofouling. *Colloid Surface B* **18**(3–4): 261–275 (2000)

[13] Goda T, Ishihara K, Miyahara Y. Critical update on 2-methacryloyloxyethyl phosphorylcholine (MPC) polymer science. *J Appl Polym Sci* **132**(16): app.41766 (2015)

[14] Shiomoto S, Inoue K, Higuchi H, Nishimura S N, Takaba H, Tanaka M, Kobayashi M. Characterization of hydration water bound to choline phosphate-containing polymers. *Biomacromolecules* **23**(7): 2999–3008 (2022)

[15] Yang L M, Zhao X D, Ma Z F, Ma S H, Zhou F. An overview of functional biolubricants. *Friction* **11**(1): 23–47 (2023)

[16] Kobayashi M, Terayama Y, Hosaka N, Kaido M, Suzuki A, Yamada N, Torikai N, Ishihara K, Takahara A. Friction behavior of high-density poly(2-methacryloyloxyethyl phosphorylcholine) brush in aqueous media. *Soft Matter* **3**(6): 740–746 (2007)

[17] Tairy O, Kampf N, Driver M J, Armes S P, Klein J. Dense, highly hydrated polymer brushes *via* modified atom-transfer-radical-polymerization: Structure, surface interactions, and frictional dissipation. *Macromolecules* **48**(1): 140–151 (2015)

[18] Raviv U, Giasson S, Kampf N, Gohy J F, Jérôme R, Klein J. Lubrication by charged polymers. *Nature* **425**(6954): 163–165 (2003)

[19] Zhang J H, Su Y J, Wu J, Wang H D. Recent advances in ocular lubrication. *Friction* **12**(9): 1929–1954 (2024)

[20] Yang L M, Zhao X D, Liao X Z, Wang R, Fan Z J, Ma S H, Zhou F. Biomimetic chitosan-derived bifunctional lubricant with superior antibacterial and hydration lubrication performances. *J Colloid Interf Sci* **629**: 859–870 (2023)

[21] Meng S, Liu Z J, Zhong W, Wang Q H, Du Q G. Phosphorylcholine modified chitosan: Appetent and safe material for cells. *Carbohydr Polym* **70**(1): 82–88 (2007)

[22] Zheng Y W, Yang J L, Liang J, Xu X Y, Cui W G, Deng L F, Zhang H Y. Bioinspired hyaluronic acid/phosphorylcholine polymer with enhanced lubrication and anti-inflammation. *Biomacromolecules* **20**(11): 4135–4142 (2019)

[23] Lin W F, Mashiah R, Seror J, Kadar A, Dolkart O, Pritsch T, Goldberg R, Klein J. Lipid-hyaluronan synergy strongly reduces intrasynovial tissue boundary friction. *Acta Biomater* **83**: 314–321 (2019)

[24] Goda T, Konno T, Takai M, Moro T, Ishihara K. Biomimetic phosphorylcholine polymer grafting from polydimethylsiloxane surface using photo-induced polymerization. *Biomaterials* **27**(30): 5151–5160 (2006)

[25] Iwasaki Y, Takamiya M, Iwata R, Yusa S I, Akiyoshi K. Surface modification with well-defined biocompatible triblock copolymers Improvement of biointerfacial phenomena on a poly (dimethylsiloxane) surface. *Colloid Surface B* **57**(2): 226–236 (2007)

[26] Zhang K, Yang J L, Sun Y L, He M R, Liang J, Luo J, Cui W G, Deng L F, Xu X Y, Wang B, et al. Thermo-sensitive dual-functional nanospheres with enhanced lubrication and drug delivery for the treatment of osteoarthritis. *Chemistry* **26**(46): 10564–10574 (2020)

[27] Ishihara K, Mu M W, Konno T. Water-soluble and amphiphilic phospholipid copolymers having 2-methacryloyloxyethyl phosphorylcholine units for the solubilization of bioactive compounds. *J Biomater Sci Polym Ed* **29**(7–9): 844–862 (2018)

[28] Nguyen T L, Kawata Y, Ishihara K, Yusa S I. Synthesis of amphiphilic statistical copolymers bearing methoxyethyl and phosphorylcholine groups and their self-association behavior in water. *Polymers* **12**(8): 1808 (2020)

[29] Zhao J, Chai Y D, Zhang J, Huang P F, Nakashima K, Gong Y K. Long circulating micelles of an amphiphilic random copolymer bearing cell outer membrane phosphorylcholine zwitterions. *Acta Biomater* **16**: 94–102 (2015)

[30] Mu M W, Konno T, Inoue Y, Ishihara K. Solubilization of poorly water-soluble compounds using amphiphilic phospholipid polymers with different molecular architectures. *Colloid Surface B* **158**: 249–256 (2017)

[31] Chantasirichot S, Inoue Y, Ishihara K. Amphiphilic triblock phospholipid copolymers bearing phenylboronic acid groups for spontaneous formation of hydrogels with tunable mechanical properties. *Macromolecules* **47**(9): 3128–3135 (2014)

[32] Yusa S I, Fukuda K, Yamamoto T, Ishihara K, Morishima Y. Synthesis of well-defined amphiphilic block copolymers having phospholipid polymer sequences as a novel biocompatible polymer micelle reagent. *Biomacromolecules* **6**(2): 663–670 (2005)

[33] Zhao W W, Wang H, Han Y, Wang H M, Sun Y L, Zhang H Y. Dopamine/phosphorylcholine copolymer as an efficient joint lubricant and ROS scavenger for the treatment of osteoarthritis. *ACS Appl Mater Inter* **12**(46): 51236–51248 (2020)

[34] Iwasaki Y, Ishihara K. Cell membrane-inspired phospholipid polymers for developing medical devices with excellent biointerfaces. *Sci Technol Adv Mater* **13**(6): 064101 (2012)

[35] Kyomoto M, Moro T, Saiga K, Hashimoto M, Ito H, Kawaguchi H, Takatori Y, Ishihara K. Biomimetic hydration lubrication with various polyelectrolyte layers on cross-linked polyethylene orthopedic bearing materials. *Biomaterials* **33**(18): 4451–4459 (2012)

[36] Raviv U, Perkin S, Laurat P, Klein J. Fluidity of water confined down to subnanometer films. *Langmuir* **20**(13): 5322–5332 (2004)

[37] Klein J. Hydration lubrication. *Friction* **1**(1): 1–23 (2013)

[38] Fu D C, Lu Y F, Peng Z Y, Zhong W B. A zwitterionic hydrogel with a surprising function of increasing the ionic conductivity of alkali metal chloride or sulfuric acid water-soluble electrolyte. *J Mater Chem A* **11**(25): 13543–13551 (2023)

[39] Ishihara K, Nomura H, Mihara T, Kurita K, Iwasaki Y, Nakabayashi N. Why do phospholipid polymers reduce protein adsorption. *J Biomed Mater Res* **39**(2): 323–330 (1998)

[40] Ishihara K, Mu M W, Konno T, Inoue Y, Fukazawa K. The unique hydration state of poly(2-methacryloyloxyethyl phosphorylcholine). *J Biomater Sci Polym Ed* **28**(10–12): 884–899 (2017)

[41] Ma L R, Gaisinskaya-Kipnis A, Kampf N, Klein J. Origins of hydration lubrication. *Nat Commun* **6**: 6060 (2015)

[42] Chen M, Briscoe W H, Armes S P, Cohen H, Klein J. Polyzwitterionic brushes: Extreme lubrication by design. *Eur Polym J* **47**(4): 511–523 (2011)

[43] Kinugasa S, Nakahara H, Fudagawa N, Koga Y. Aggregative behavior of poly(ethylene oxide) in water and methanol. *Macromolecules* **27**(23): 6889–6892 (1994)

[44] Devanand K, Selser J C. Asymptotic behavior and long-range interactions in aqueous solutions of poly(ethylene oxide). *Macromolecules* **24**(22): 5943–5947 (1991)

[45] Fu Z L, Santore M M. Kinetics of competitive adsorption of PEO chains with different molecular weights. *Macromolecules* **31**(20): 7014–7022 (1998)

[46] Mubarekyan E, Santore M M. Energy barrier to self-exchange between PEO adsorbed on silica and in solution. *Macromolecules* **34**(21): 7504–7513 (2001)

[47] Flood C, Cosgrove T, Howell I, Revell P. Effects of electrolytes on adsorbed polymer layers: Poly(ethylene oxide)–silica system. *Langmuir* **22**(16): 6923–6930 (2006)

[48] Müller M, Lee S, Spikes H A, Spencer N D. The influence of molecular architecture on the macroscopic lubrication properties of the brush-like co-polyelectrolyte poly(L-lysine)-g-poly(ethylene glycol) (PLL-g-PEG) adsorbed on oxide surfaces. *Tribol Lett* **15**(4): 395–405 (2003)

[49] Yan Y F, Sun T, Zhang H B, Ji X L, Sun Y L, Zhao X, Deng L F, Qi J, Cui W G, Santos H A, et al. *Euryale ferox* seed-inspired superlubricated nanoparticles for treatment of osteoarthritis. *Adv Funct Mater* **29**(4): 1807559 (2019)

[50] Yi X B, Xu H Y, Jin G, Lu Y, Chen B Q, Xu S F, Shi J Q, Fan X L. Boundary slip and lubrication mechanisms of organic friction modifiers with effect of surface moisture. *Friction* **12**(7): 1483–1498 (2024)

[51] Pettersson T, Naderi A, Makuska R, Claesson P M. Lubrication properties of bottle-brush polyelectrolytes: An AFM study on the effect of side chain and charge density. *Langmuir* **24**(7): 3336–3347 (2008)

[52] Iruthayaraj J, Olanya G, Claesson P M. Viscoelastic properties of adsorbed bottle-brush polymer layers studied by quartz crystal microbalance: Dissipation measurements. *J Phys Chem C* **112**(38): 15028–15036 (2008)

[53] Dėdinaitė A. Biomimetic lubrication. *Soft Matter* **8**(2): 273–284 (2012)

[54] Ueda T, Oshida H, Kurita K, Ishihara K, Nakabayashi N. Preparation of 2-methacryloyloxyethyl phosphorylcholine copolymers with alkyl methacrylates and their blood compatibility. *Polym J* **24**(11): 1259–1269 (1992)

[55] Sato T, Miyoshi T, Seno M. Kinetic study on the radical polymerization of 2-methacryloyloxyethyl phosphorylcholine. *J Polym Sci A Polym Chem* **38**(3): 509–515 (2000)

[56] Ishihara K, Tsuji T, Kurosaki T, Nakabayashi N. Hemocompatibility on graft copolymers composed of poly(2-methacryloyloxyethyl phosphorylcholine) side chain and poly(n-butyl methacrylate) backbone. *J Biomed Mater Res* **28**(2): 225–232 (1994)

[57] Bhuchar N, Deng Z C, Ishihara K, Narain R. Detailed study of the reversible addition–fragmentation chain transfer polymerization and co-polymerization of 2-methacryloyloxyethyl phosphorylcholine. *Polym Chem* **2**(3): 632–639 (2011)

[58] Liu Y H, Inoue Y, Sakata S, Kakinoki S, Yamaoka T, Ishihara K. Effects of molecular architecture of phospholipid polymers on surface modification of segmented polyurethanes. *J Biomater Sci Polym Ed* **25**(5): 474–486 (2014)

[59] Jurkūnas M, Klimkevičius V, Uscilaitė A, Makuška R. Synthesis of superhydrophilic gradient-like copolymers: Kinetics of the RAFT copolymerization of methacryloyloxyethyl phosphorylcholine with PEO methacrylate. *Eur Polym J* **183**: 111764 (2023)

[60] Xi Y W, Choi C H, Chang R, Kaper H J, Sharma P K. Tribology of pore-textured hard surfaces under physiological conditions: Effects of texture scales. *Langmuir* **39**(19): 6657–6665 (2023)

[61] Ren K, Reina Mahecha M A, Hübner M, Cui Z W, Kaper H J, van der Veen H C, Sharma P K. Tribology of enzymatically degraded cartilage mimicking early osteoarthritis. *Friction* **11**(9): 1724–1740 (2023)

[62] Ren K, Wan H P, Kaper H J, Sharma P K. Dopamine-conjugated hyaluronic acid delivered via intra-articular injection provides articular cartilage lubrication and protection. *J Colloid Interf Sci* **619**: 207–218 (2022)

[63] Wan H P, Ren K, Kaper H J, Sharma P K. Cartilage lamina splendens inspired nanostructured coating for biomaterial lubrication. *J Colloid Interf Sci* **594**: 435–445 (2021)

[64] Majd S E, Rizqy A I, Kaper H J, Schmidt T A, Kuijer R, Sharma P K. An *in vitro* study of cartilage–meniscus tribology to understand the changes caused by a meniscus implant. *Colloid Surf B* **155**: 294–303 (2017)

[65] Jurkūnas M, Talaikis M, Klimkevičius V, Pudžaitis V, Niaura G, Makuška R. Diblock copolymers of methacryloyloxyethyl phosphorylcholine and dopamine methacrylamide: Synthesis and real-time adsorption dynamics by SEIRAS and RAIRS. *Langmuir* **40**(11): 5945–5958 (2024)

[66] Klimkevicius V, Makuska R. Successive RAFT polymerization of pol y(ethylene oxide) methyl ether methacrylates with different length of PEO chains giving diblock brush copolymers. *Eur Polym J* **86**: 94–105 (2017)

[67] Chen H, Sun T, Yan Y F, Ji X L, Sun Y L, Zhao X, Qi J, Cui W G, Deng L F, Zhang H Y. Cartilage matrix-inspired biomimetic superlubricated nanospheres for treatment of osteoarthritis. *Biomaterials* **242**: 119931 (2020)

[68] Zhang H Y, Wang Y, Vasilescu S, Gu Z B, Sun T. Bio-inspired enhancement of friction and adhesion at the polydimethylsiloxane-intestine interface and biocompatibility characterization. *Mater Sci Eng C* **74**: 246–252 (2017)

[69] Sun T, Sun Y L, Zhang H Y. Phospholipid-coated mesoporous silica nanoparticles acting as lubricating drug nanocarriers. *Polymers* **10**(5): 513 (2018)

[70] Chan S M T, Neu C P, DuRaine G, Komvopoulos K, Reddi A H. Atomic force microscope investigation of the boundary-lubricant layer in articular cartilage. *Osteoarthr Cartil* **18**(7): 956–963 (2010)

[71] Katta J, Jin Z M, Ingham E, Fisher J. Biotribology of articular cartilage: A review of the recent advances. *Med Eng Phys* **30**(10): 1349–1363 (2008)

[72] Caligaris M, Ateshian G A. Effects of sustained interstitial fluid pressurization under migrating contact area, and boundary lubrication by synovial fluid, on cartilage friction. *Osteoarthr Cartil* **16**(10): 1220–1227 (2008)

[73] Soltz M A, Ateshian G A. Experimental verification and theoretical prediction of cartilage interstitial fluid pressurization at an impermeable contact interface in confined compression. *J Biomech* **31**(10): 927–934 (1998)

[74] Wang Y, Zhai W J, Zhang H Y, Cheng S J, Li J H. Injectable polyzwitterionic lubricant for complete prevention of cardiac adhesion. *Macromol Biosci* **23**(4): 2200554 (2023)

[75] Klimavicius V, Klimkevicius V, Aidas K, Balčiūnas S, Banys J, Makuska R, Balevicius V. Fine structural features and proton conduction in zwitterionic poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC): Multinuclear solid-state NMR, impedance and FTIR spectroscopy study. *React Funct Polym* **192**: 105727 (2023)

[76] Naderi A, Iruthayaraj J, Pettersson T, Makuška R, Claesson P M. Effect of polymer architecture on the adsorption properties of a nonionic polymer. *Langmuir* **24**(13): 6676–6682 (2008)

[77] Coles J M, Chang D P, Zauscher S. Molecular mechanisms of aqueous boundary lubrication by mucinous glycoproteins. *Curr Opin Colloid In* **15**(6): 406–416 (2010)

[78] Han M Y, Silva S M, Lei W W, Quigley A, Kapsa R M I, Moulton S E, Greene G W. Adhesion and self-assembly of lubricin (PRG4) brush layers on different substrate surfaces. *Langmuir* **35**(48): 15834–15848 (2019)

[79] Lin W F, Klein J. Recent progress in cartilage lubrication. *Adv Mater* **33**(18): 2005513 (2021)

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