Tuned Surface and Mechanical Properties of Polymeric Film Prepared by Random Copolymers Consisting of Methacrylate-POSS and 2-(Methacryloyloxy)ethyl Phosphorylcholine

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Macromolecular Chemistry and Physics

Tuned Surface and Mechanical Properties of Polymeric Film Prepared by Random Copolymers Consisting of Methacrylate-POSS and 2-(Methacryloyloxy)ethyl Phosphorylcholine

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Abstract: Poly(2-(methacryloyloxy)ethyl phosphorylcholine) (PMPC) is known as biocompatible polymers. Copolymerization of MPC and hydrophobic monomers is a general approach to enabling us to give bio-inert functions toward solid materials via the surface coating. However, due to the amorphous nature and super hydrophilicity of the MPC-based copolymers, both the surface and mechanical properties have not been controlled for biomedical applications. Here, we show that the modulated mechanical property and surface wettability of the MPC-based copolymers by using a polyhedral oligomeric silsesquioxane (POSS) methacrylate. MPC was copolymerized with POSS methacrylates bearing different vertex groups of ethyl (C_2H_5), hexayl (C_6H_{13}) and octayl (C_8H_{17}) via radical polymerization. We found that only the C_2H_5-POSS induced the increased mechanical strength, low surface wettability, and cellular attachment, suggesting that the C_2H_5-POSS moiety restricted the motion of PMPC chain. We anticipate our finding to be tuned for both surface and bulk functions of PMPC for biomedical applications.

1. Introduction

Phospholipids draw great interest in application for biomedical science as one of the major components of lipid bilayer in cellular membrane. Due to the great biocompatibility of the phosphorylcholine group, this moiety has been introduced to the design of synthetic polymers for biomedical applications. The representative one is 2-(methacryloyloxy)ethyl phosphorylcholine (MPC) polymers that have been developed by Ishihara *et al.*[1,2] The phosphorylcholine group of 2-(methacryloyloxy)ethyl phosphorylcholine (MPC) is one of the component of cell membranes [3]. The zwitterionic nature of phosphorylcholin (PC) group in the side chain of MPC is responsible for its bioinert nature[4]. By copolymerization of MPC with the other monomers, those functions and physicochemical properties can be controlled for modulationg surface and/or interface properties. So far, MPC polymers copolymerized with hydrophobic monomers have been widely applyed for biomedical applications including surface coating for blood compatible materials[5, 6], a film exhibited the elastic properties with high tensile strength[7], oxygen sensing membrane[8], and polymeric micelles for controlled release of anticancer drugs[9].

Polyhedral oligosilsesquioxane (POSS) refers to a well-defined organic/inorganic hybrid material, whose chemical structure follows the basic composition of $R_nSi_nO_{1.5n}$. Small size silica-like cage POSS shows excellent compatibility to most of the organic polymers via blending, graft copolymerization and polymerization [10,11]. It was reported that incorporation of POSS provides enhanced mechanical property, thermal stability, anti-biodegradable property and biocompatibility. Due to hydrophobic nature of POSS cage, POSS-based amphiphilic polymers have been studied by introducing the POSS moiety to the ends of hydrophilic chain such as poly (ethylene oxide) (PEO) and poly (ethylene glycol) (PEG) [12,13], resulting in the self-assembled micelle and vesicle in solutions and solvent-sensitive self-association behavior [10]. Another approach to preparing POSS-based amphiphilic polymers are copolymerization of POSS-based monomers. Since the reactivity for POSS monomers is high, various kinds of copolymers prepared with methyl methacrylate[14,15], n-butyl acrylate[16] and styrene[17,18]. Unlike physical blend of POSS moiety into a polymer matrix, the random POSS copolymers does not induce aggregation and crystallization, leading to molecular-level-dispersion of the POSS moiety through whole polymer matrix. Typical characteristic of the random POSS copolymers includes less the decreased rubbery plateau modulus, meaning the increased entanglement density[18], which depends on the vertex (R) groups at the corners of the POSS moiety such as isobutjyl, cyclohexyl, and cyclopentyl groups[19]. Recently, a new concept of polymer hybrids has been suggested: Incorporation of inorganic component with domain size at the nano or molecular scale into the polymer matrix produces organic-inorganic polymer hybrids, in which structural unit consisting of various groups of elements is termed as "*element block*" [20]. Design and synthesis of new element blocks and polymerization of those blocks creates new polymeric materials with improved material properties. By considering POSS as an element block, organic inorganic hybrid at molecular level can be prepared and applied to improve the property of biomaterials.

Haemocompatibility is an essential requirement of cardiovascular implant materials. Among them, nano-composite polymers have been extensively studied and found unique characteristics at blood-biomaterial interface. The POSS-containing polymers have been investigated in the field of biomaterials[13]. Recent study showed that small diameter coronary artery bypass grafts composed of POSS-copolymerized with poly(carbonate ures)urethane (POSS-PCU) improved the thermal and mechanical properties, resulting in elimination of their apparent disadvantages. In the view points of good haemocompatible polymers, a MPC-based amphiphilic polymer is a promising candidate to fabricate fibers with excellent hemocompatibility[21]. Although the MPC-based amphiphilic polymer is promising for biomedical applications as mentioned above, the improved thermal and mechanical properties are still challenging issues toward the developments as biomaterials.

In this study, POSS methacrylates bearing different vertex (R-) groups such as ethyl, hexayl and octayl were co-polymerized with MPC via radical polymerization. The effect of the R-group in the POSS moiety was evaluated in terms of thermal, mechanical, physical and surface properties of the copolymer. We found that thermal and mechanical strengths were increased by employing only the ethyl (R= C_2H_5)-POSS in the co-polymers. Solubility characteristics of the copolymers in various solvents were evaluated, and observation is provided on how this R-group in the POSS moiety of copolymer influenced the wettability and hydrophilicity when coated on the surface. This study suggests a new approach to enhancing and tuning the properties of MPC, which is of advantage when using these copolymers as surface coating materials with improved thermal and mechanical property.

2. Results and Discussion

2.1. Synthesis and characterization of POSS-MPC copolymers

Ethyltrimethoxysilane-based POSS-methacrylate (**2a**), hexyltrimethoxysilane-based POSS-methacrylate (**2b**) and trimethoxyoctylsilane-based POSS-methacrylate (**2c**) were prepared by using silsesquioxane partial cages (**1a-c**) and 3-methacryloxypropyl trichlorosilane (See **SchemeS1** in Supporting information). The POSS-MPC copolymers **(3a-c; Figure 1)** were prepared by conventional radical polymerization using AIBN as an initiator. The solubility of **3a-c** in various solvents was compared to check the influence of aliphatic chain length of the POSS moiety (**Table S1** in Supporting information). Solubility of **3a**, **3b** and **3c** in water, methanol and ethanol was abruptly decreased in comparison to Poly MPC. This might be due to strong interaction between the incorporated POSS moiety and phosphorylcholine group, which is responsible for solubility in water and the hydrophobic region is exposed on the solid polymer surface even in water [22]. The molecular weight obtained from GPC summarized in the **Table 1**. Number-average molecular weight (M_n) of all the polymers is in the range of 10^4. In the case of **3a**, the molecular weight was found to be lower than other two copolymers, suggesting that the increased copolymerization ratio of **2a**, which was calculated by ^{1}H-NMR, affected the propagation and termination process of the radical polymerization.

(Insert **Figure 1**)

Compositions of **3a-c** were analyzed by the XPS spectra (**Table S2** in Supporting information). The peaks of the carbon atom region (C_{1s}) at 285.0 eV in all the copolymers corresponded to the neutral carbon. The peak of the phosphorus (P_{2p}) atom region (corresponding to the phosphate group) was detected at 133.0 eV and the nitrogen (N_{1s}) atom region corresponding to protonated ammonium group was detected at 403.0 eV [23,24]. The appearance of the Si 2_p (101 eV) and Si 2_s (152 eV) was confirmed, indicating the presence of Si. From these results, the successful incorporation of POSS moiety in **3a-c** was confirmed.

The obtained copolymers were characterized by thermal analysis (**Table 1**). With an incorporation of 1mol % POSS, T_g of **3a-c** increased in the order of **3a** > 3c ≈ **3b**. In the case of **3a**, T_g increased to 11 ºC, which is 8 ºC higher than that of control (poly MPC). Since the thermal property of polymer is primarily associated with their structural orientation, the POSS moiety incorporated to the MPC chains is likely to hinder the motion of MPC chain in the polymer matrix to a large extent. This would be the main reason for remarkable improvement in T_g [25]. In all the three copolymers, 1 mol % POSS was used and all the three copolymers showed a remarkable improvement in T_g. To further investigate the mechanism of T_g increase, the FTIR characterization of the three copolymers and poly MPC were carried out. The poly MPC showed the carbonyl (C=O) and choline ($-N^+(CH_3)_3$) absorption at ~1724 cm^{-1} and 966 cm^{-1} respectively. In the case of **3a**, a strong shoulder peak appeared at low frequency (1717 cm^{-1}), and the several other shoulder peaks were observed in the carbonyl-related region

(**Figure S2** in Supporting information), indicating strong dipole-dipole interaction between the C_2H_5-POSS and the carbonyl group of the MPC part: Dipole-dipole interaction surpasses the diluting effect of POSS and helping in contribution for increasing T_g [25-27]. In the case of **3c**, the broad absorption shoulder appeared at 1725 cm^{-1}, indicating the interaction between C_8H_{17}-POSS and the carbonyl group of the MPC part. When the alkyl chain length was middle one (**3b**), the absorption maximum tends to shift toward higher frequency (1728 cm^{-1}). Since the molecular weight of **3b** and **3c** (>200,000 g mol^{-1}) was much higher than that of **3a** (~90,000 g mol^{-1}) (**Table 1)**, high molecular weight-related topological restriction of **3b** and **3c** is considered to be governed by chain movement [28]. On the other hand, as seen in the IR spectrum of **3a** in **Figure S2**, various energy states of the carbonyl region suggest that the carbonyl group of MPC part was attracted by inhomogeneously distributed C_2H_5-POSS moiety in the MPC-based polymeric backbone.

From TGA thermograms, four step degradations at ~139, ~241, ~349 and ~397 ºC were observed. These results suggest that incorporation of inorganic POSS cores is increasing the thermal stability and the temperature at the first degradation ($T_{Initiation)}$ (poly MPC ~137 ºC) to 161 ºC (**3a**), 144 ºC (**3b**), 141 ºC (**3c**) [25]. XPS study was performed on the TGA char yield, and it was found that there was no trace of Si in the three copolymers after 500ºC.

X-ray diffraction patterns of Poly MPC and **3a-c** were taken at room temperature (**Figure. S3** in Supporting information). The XRD pattern for Poly MPC indicated the amorphous broad peak pattern. As a reference, the XRD pattern of **1a** (partial cage) was measured, and the obtained main reflections at around 8-11°, which correspond to lattice spacing of 11-8Å, was very similar to those recently reported for other POSS molecules [29]. In the case of **3a-c**, such the main reflections attributed to POSS moiety was not observed, and those were similar structure of poly MPC. These results indicate no crystallization of POSS moiety in **3a-c**. Also, the intensity of the peak at $2\theta \approx 20^{o}$, attributed to the amorphous halo of poly MPC, decreased due to enlarging the inter chain correlation distance and inter-side-group correlation [30].

2.2. Bulk property of the copolymer-casted films

In order to assess the bulk properties of **3a-c** in relation to the increased T_g (**Table 1**), tensile and compression tests were performed by using cast films. Although we tried to prepare the bulk film only made by **3a-c**, it was very hard to prepare the bulk film. **Figure 2** showed the Young's modulus and tensile strength calculated from the results of tress-strain curves (**Figure S4** in Supporting information). It was found that both Young's modulus and tensile strength of **3a** increased significantly in comparison with the other copolymers. It is noted that **3b** could not be measured those values due to weak mechanical strength. Compression testing results (**Figure S5 and S6** in Supporting information) also supported the results of **Figure 2**: Incorporation of the C_2H_5-POSS moiety increased the Young's modulus of **3a.** These results suggest that the mechanical properties are well correlated with the results of T_g in **Table 1** and FTIR spectra (**Figure S2** in Supporting information): The main reason for increase in mechanical property of **3a** was due to the interaction between C_8H_{17}-POSS and the carbonyl group of the MPC part. Taking the Young's modulus data calculated from tensile and compression tests, FT-IR, and XRD data into account, inhomogeneously distributed the C_2H_5-POSS moiety in **3a** matrix was located in the nanometer scale, leading to better Young's modulus [7,11,31-34]. The long alkyl side chain of POSS in **3b** and **3c** matrices was not favorable to tangle with MPC polymeric chains in terms of the decreased elasticity of the material [11, 35].

(Insert **Figure 2**)

2.3. Film Coating

Surface characterization of the coated film of **3a-c** was performed using XPS (**Table S3** in Supporting information). Peaks for Si 2_p (101 eV) and Si 2_s (152 eV) were observed on the surface of all the copolymers-coated films. Atomic concentration (%) analysis showed that Si concentration higher on the surface of **3a**-coated film, indicating the presence of POSS moiety on the surface. Surface morphology of the coated films was observed by SEM. Typically, 1% w/v **3a** solution concentration used for the coating provided smooth wave-like surface, but when higher % solution (10% w/v) concentration was used for coating, it provided liner cracked surface (**Figure S7** in Supporting information).

2.4. Surface property: wettability, protein adsorption and cellar attachment

From the results of solubility testing (**Table S1** in Supporting information), we hypothesized that **3a-c** exhibits much hydrophobic surface due to the restricted motion of the MPC moiety. The results of static contact angle (**Figure 3A**) showed that the concentration for the spin coating should be over 5% w/v, because the value for poly MPC decreased significantly over 5% w/v, suggesting that each copolymer covered the whole film area over 5% w/v. It was suggested that the highest contact angle of the **3a**-coated surface supported our hypothesis: The C_2H_5 moiety was preferably located on the surface due to the restricted motion. The static contact angle was also measured using 0.1 M phosphate buffered saline (PBS) at pH 7.4 to evaluate the wettability of copolymer coated surface in a physiological environment (**Figure S8** and **S9** in Supporting Information). The contact angle of **3a** showed highest value at 5 % w/v, which was higher than the value in pure water. This may be due to the presence of inorganic salt in PBS to form hydrophobic region (C_2H_5-POSS moiety) [22]. However, the value was decreased when **3a** was coated at 10 % w/v solution concentration. Due to the cracked surface of **3a** at the 10 % w/v concentration (See **Figure S7**), the surface was possibly unstable either in pure water and in PBS. In the case of **3b** and **3c**, the contact angle value showed over

100° when the 10 % w/v solution was used (See also **Figure S9 (iv)** and **(v)** in Supporting Information). These phenomena suggest that the surface of **3b** and **3c**-coated film at the high concentration is sensitive to the salt-containing aqueous environment, which is likely to be related to the chain entanglement-governed movement of the polymeric chain of **3b** and **3c**, as mentioned before on the section 2.1. Overall, the **3a**-coated surface at 1 and 5% w/v exhibited relatively hydrophobic one in both pure water and PBS.

In order to assess the correlation between the surface wettability and protein adsorption, amount of protein adsorption on the film coated with 1 and 5% w/v copolymer solutions were quantified using BSA as a model protein. The BSA adsorption was only observed in **3a**-coated film and increased with an increase in coating thickness (**Figure 3B**). This phenomenon suggests that the hydration layer surrounding the PC group in poly MPC, which gives the resistance to the protein adsorption, was disrupted by the C_2H_5-POSS moiety on the water-polymer interface [22-24,35]. Taking the surface hydrophobicity of **3a**-coated film into account, the C_2H_5-POSS moiety is considered to be exposed on the interface. This result was strongly correlated with the surface wettability 0.1 M PBS (pH 7.4) (**Figure S8** in Supporting Information). Stability of the surface coating during the incubation in 0.1 M PBS (pH 7.4) was investigated by XPS analysis (**Table S4** in Supporting Information). Although the percentage of Si2p decreased in comparison with that of before the incubation, all the copolymers were found to be still remained, suggesting the presence of the copolymers on the surface during the protein adsorption study.

Cell attachment on the **3a**-coated surface was performed using NIH 3T3 cell line, in order to check how the exposed C_2H_5-POSS moiety affected to cellular interaction. After 24 and 48 hr of incubation at 37 ºC, the morphology of the cells were observed under digital inverted microscope (**Figure 3C**). The number of cells were increased after 24 hr. but the cells did not spread out on the **3a**-coated surface. After 48 hr., typical spreading morphology of the cells with membrane extension were observed. This phenomenon supported that the unique hydration state of poly MPC chain that resists the protein adsorption and cell adhesion get affected by the incorporation of C_2H_5-POSS moiety into the polymeric matrix.

(Insert **Figure 3**)

3. Conclusions

We found that C_2H_5-POSS-based random copolymer in combination with MPC showed very unique surface and bulk properties. The hydrophobic region dispersed in the poly MPC matrix provides the controlled protein adsorption and cell attachment. In contest of the investigation conducted herein, it can be concluded that C_2H_5-POSS-based random copolymer fulfill all requisite characteristics needed to develop it for further biomedical application.

Supporting Information

Supporting Information is available from the Wiley Online Library

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Keywords: copolymerization, polyhedral oligomeric silsesquioxane, 2-(methacryloyloxy)ethyl phosphorylcholine, surfaces, biomaterials

References

[1] Y. Iwasaki, K. Ishihara, *Anal. Bioanal. Chem.* **2005**, *381*, 534-546.

[2] K. Ishihara, H. Nomura, T. Mihara, K. Kurita, Y. Iwasaki, N. Nakabayashi, *J. Biomed. Mater. Res., Part A* **1998**, *39*, 323-330.

[3] K. Fukuda, R. Enomoto, K. Ishihara, Y. Morishima, S. Yusa, *Polymers* **2014**, *6*, 846-859.

[4] T. Goda, K. Ishihara, Y. Miyahara, *J. Appl. Polym. Sc.* **2015**, *132*, 41766.

[5] T. Ueda, H. Oshida, K. Kurita, K. Ishihara, N. Nakabayashi, *Polym. J.* **1992**, *24*, 1259–1269.

[6] S. P. Ho, N. Nakabayashi, Y. Iwasaki, T. Boland, M. LaBerge, *Biomaterials* **2003**, *24*, 5121-5129.

[7] W. Sirithep, Y. Narita, Y. Nagase, *Trans. Mat. Res. Soc. Japan* **2013**, *38,* 473-476.

[8] K. H. Chae, Y. M. Jang, Y.H. Kim, O. Sohn, J. I. Rhee, *Sensors and Actuators B* **2007**, *124*, 153-160.

[9] J. Xu, J. Ji, W. Chen, D. Fan, Y. Sun, J. Shen, *Eur. Polym. J.* **2004**, *40*, 291-298.

[10] J. Wu, P. Mather, *J. of Macromol. Sci., Part C: Polm. Rev.* **2009**, *49*, 25-63.

[11] S. Kuo, F. Chang, *Prog. Polm. Sci.* **2011**, *36*, 1649-1696.

[12] G. Li, L. Wang, H. Ni, C. Pittman Jr., *J. Inorg. Organometa. Polym.* **2001**, *11*, 3.

[13] H. Ghanbari, B. G. Cousins, A. M. Seifalian, *Macromol. Rapid Commun.* **2011**, *32*, 1032-1046.

[14] E.T. Kopesky, T.S. Haddad, R.E. Cohen, G.H. McKinley, *Macromolecules* **2004**, *37*, 8992–9004.

[15] H.Y. Xu, B.H. Yang, J.F. Wang, S.Y. Guang, C. *J.* Li, *Polym. Sci. Polm. Chem.* **2007**, *45*, 5308–5317.

[16] J. Pyun, K. Matyjaszewski, J. Wu, G. M. Kim, S.B. Chun, P.T. Mather, *Polymer* **2003**, *44*, 2739–2750.

[17] A. Romo-Uribe, P.T. Mather, T.S. Haddad, J.D. Lichtenhan, *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 1857–1872.

[18] J. Wu, T.S. Haddad, G.M. Kim, P.T. Mather, *Macromolecules* **2007**, *40,* 544–554.

[19] J. Wu, T.S. Haddad, P.T. Mather, *Macromolecules* **2009**, *42*, 1142-1152.

[20] Y. Chujo, K. Tanaka, *Bull. Chem. Soc. Jap.* **2015**, *88*, 633-643.

[21] T. Maeda, K. Hagiwara, S.Yoshida, T. Hasebe, A. Hotta, *J. Appl. Polym. Sci.* **2014,** *131*, 40606.

[22] K. Ishihara, M. Mu, T. Konno, Y. Inoue, K. Fukazawa, *J. Biomater. Sci. Polym. Ed.* **2017**, *28*, 884-899.

[23] Y. Inoue, Y. Onodera, K. Ishihara, *Colloids and Surfaces B: Biointerfaces* **2016**, *141*, 507–512.

[24] Y. Inoue, T. Nakanishi, K. Ishihara, *React. & Funct. Polym.* **2011,** *71*, 350–355.

[25] H. Xu, B. Yang, J. Wang, S. Guang, C. Li, *J. Polym. Sci.: Part A: Poly. Chem.* **2007**, *45*, 5308–5317.

[26] H. Xu, S. Kuo, J. Lee, F. Chang, *Macromolecules* **2002**, *35*, 23.

[27] O. Bianchi, J. N. Martins, C. Luvison, S. G. Echeverrigaray, C. D. Castel, R. V. B. Oliveira, *Journal of Non-Crystalline Solids* **2014**, *394-395*, 29-35.

[28] C. H. Wanke, D. Pozzo, C. Luvison, I. Krindges, C. Aguzzoli, M. R. F. Soares, O. Bianchi, *Polymer Testing* **2016**, *54,* 214-222.

[29] B. X. Fu, W. H. Zhang, B. S. Hsiao, M. Rafailovich, J. Sokolov, G. Johansson, B. B. Sauer, S. Phillips, R. Balnski, *High Perform. Polym*. **2000**, *12,* 565.

[30] J. Wu, T. S. Haddad, P. T. Mather, *Macromolecules* **2009**, *42*, 1142–1152.

[31] Pramudya, C. G. Rico, C. Lee, H. Chung, *Biomacromolecules* **2016**, *17*, 3853−3861.

[32] Y. Du, M. Yu, X. Chen, P. X. Ma, B. Lei, *ACS Appl. Mater. Interfaces* **2016**, *8,* 3079−3091.

[33] Md. Rabby, S. Jeelani, V. K. Rangari, *J. Nanomat.* **2015**, *Art. ID 894856,* 13.

[34] R. Drake, A. W. Vogl, A. W. M. Mitchell, *Gray's Anatomy E-Book: The Anatomical Basis of Clinical Practice, Nerve Biomechanics*, 3 rd ed., Churchill Livingstone, **2014**.

[35] K. Tanaka, S. Adachi, Y. Chujo, *J. Polym. Sci.: Part A: Polym. Chem.* **2009**, *47*, 5690–5697.

Figure Captions

Figure 1. Chemical structures of POSS-MPC copolymers; C_2H_5-POSS-MA MPC (**3a**), C_6H_{13}-POSS-MA MPC (**3b**) and C_8H_{17}-POSS-MA MPC (**3b**)

Figure 2. Tensile testing results of POSS-MA MPC Copolymers: Young's modulus and tensile strength

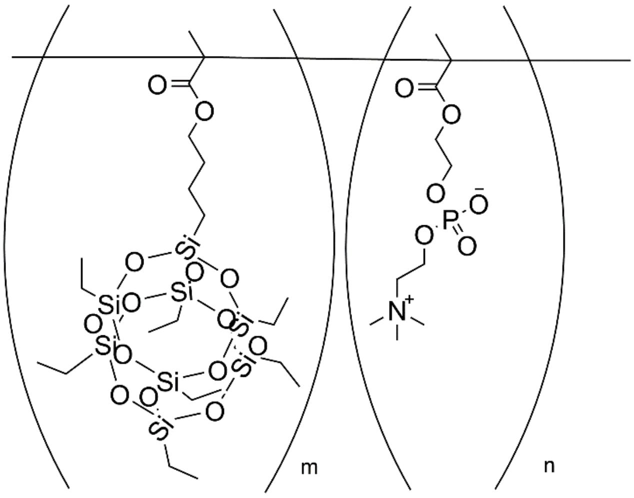
Figure 3. Surface wettability, protein adsorption and cell attachment on the copolymers coated surface. (**A**) Static contact angle of the films coated with different concentration of copolymer solutions. (**B**) BSA adsorption on the **3a-c**-coated film (coated with 1 and 5% concentration copolymer solutions). (**C**) Cell attachment on the C_2H_5-POSS-MA MPC **3a**-coated surface after 24 and 48 hr. (a and c): cell attachment on polystyrene tissue culture plate after 24 and 48 hr. respectively. (b and d) cell attachment on the **3a**-coated tissue culture plate after 24 and 48 hr. respectively.

Table 1. Chemical Composition and Thermal Properties of **3a-c**

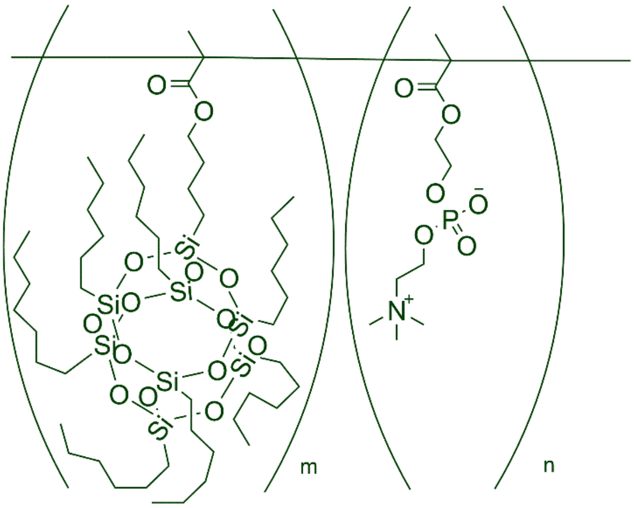
Samples		**% Mol (Feed)**	**% Mol ^{1}H-NMR**	**Molecular weights in a phosphate buffer/AcCN (9:1)**			T_g	**Char Yield**
		MPC/ R-POSS	**MPC/ R-POSS**	M_n **×10^4**	M_w **× 10^4**	M_w/ M_n	**˚C**	**%**
Poly MPC		100	100	5.7	22.5	3.3	3	30
C_2H_5-POSS-MA MPC (**3a**)		99/1	98/ 2	2.8	9.8	3.5	11	30
C_6H_{13}-POSS-MA MPC (**3b**)	①[a]	99/1	99/1	141	255	1.8	6	29
	②[a]			4.2	14.0	3.3		
	Avg.			5.1	58.6	11.5		
C_8H_{17}-POSS-MA MPC (**3c**)		99/1	ND[b]	6.1	41.1	6.8	7	29

[a] Two peak were found in GPC charts; [b] % Mole could not be determined

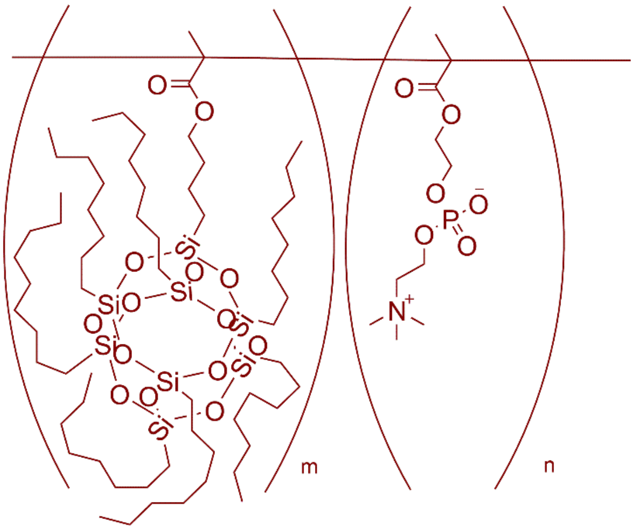
Figure 1



3a

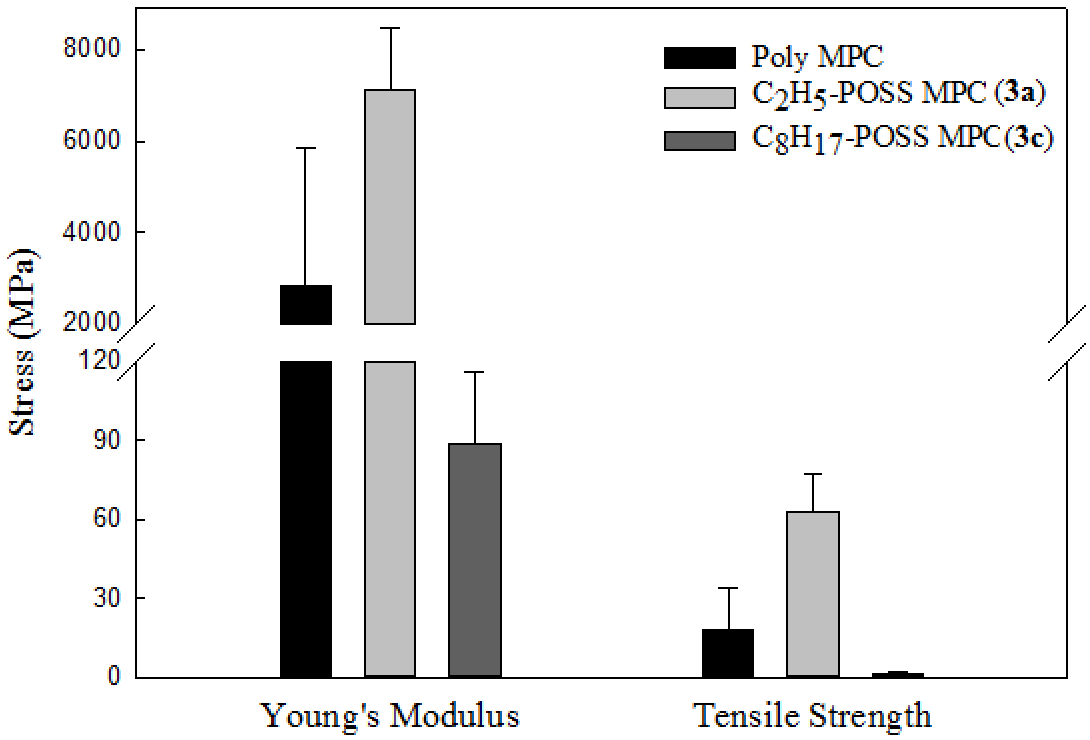


3b



3c

Figure 2



Poly MPC
C_2H_5-POSS MPC (**3a**)
C_8H_{17}-POSS MPC (**3c**)
Stress (MPa)
8000
6000
4000
2000
120
90
60
30
0
Young's Modulus
Tensile Strength

Figure 3

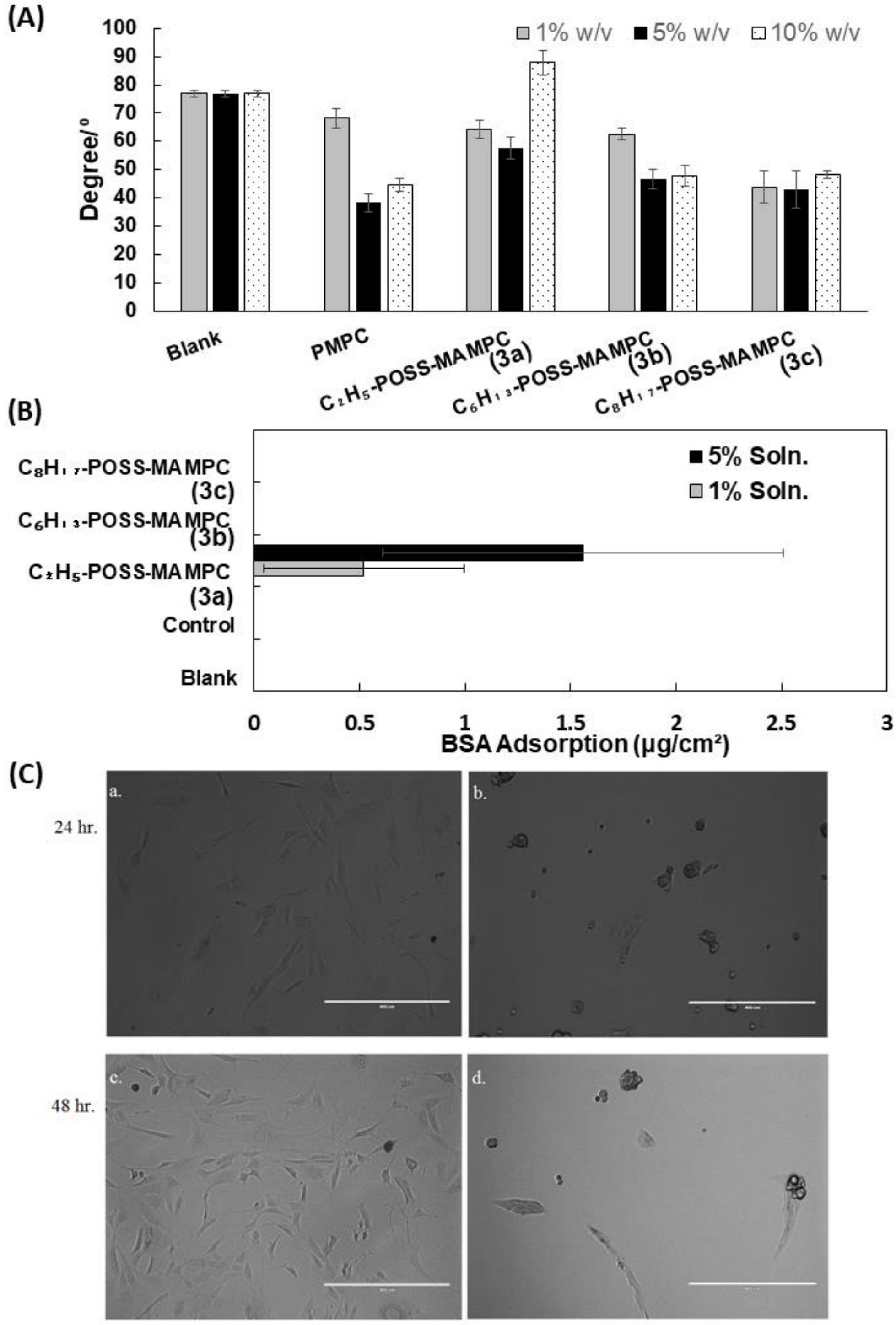

(A)
1% w/v
5% w/v
10% w/v
Degree/°
100
90
80
70
60
50
40
30
20
10
0
Blank
PMPC
C₂H₅-POSS-MAMPC (3a)
C₆H₁₃-POSS-MAMPC (3b)
C₈H₁₇-POSS-MAMPC (3c)
(B)
5% Soln.
1% Soln.
C₈H₁₇-POSS-MAMPC (3c)
C₆H₁₃-POSS-MAMPC (3b)
C₂H₅-POSS-MAMPC (3a)
Control
Blank
0
0.5
1
1.5
2
2.5
3
BSA Adsorption (μg/cm²)
(C)
24 hr.
48 hr.
a.
b.
c.
d.

Table of Contents

A random copolymer of polyhedral oligomeric silsesquioxane (POSS) methacrylate and 2-(methacryloyloxy)ethyl phosphorylcholine (MPC) improved both surface and bulk prperties. We found that only the POSS bearing ethyl group induced the increased mechanical strength, low surface wettability, and cellular attachment. We anticipate our finding to be tuned for both surface and bulk functions of PMPC for biomedical applications.

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Tuned Surface and Mechanical Properties of Polymeric Film Prepared by Random Copolymers Consisting of Methacrylate- POSS and 2-(Methacryloyloxy)ethyl Phosphorylcholine

ToC figure