

**HYDROPHILIC POLYMER BRUSH COATINGS ON
BIODEGRADABLE ALIPHATIC
POLYESTER SURFACE FOR BIOMEDICAL APPLICATIONS**

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INDIAN INSTITUTE OF TECHNOLOGY DELHI

JANUARY 2023

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**Hydrophilic polymer brush coatings on biodegradable aliphatic
polyester surface for biomedical applications**

by

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Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

JANUARY 2023

Dedicated to my family

CERTIFICATE

This is to certify that the thesis entitled, “**Hydrophilic polymer brush coatings on biodegradable aliphatic polyester surface for biomedical applications**” being submitted by **Ms. Shaifali Dhingra** to Indian Institute of Technology Delhi for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her. Ms Shaifali has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard. The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

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ACKNOWLEDGEMENTS

I wish to express my heartiest gratitude to my supervisor, **Prof. (Mrs.) Sampa Saha** for her invaluable guidance and constant encouragement. Her caring attitude and co-operation have been monumental throughout my research. Her constant inspiration and encouragement have been a great motivation for me, behind all the work which I have conducted. Through her wealth of knowledge, direction, and leadership I have been able to increase my knowledge in the area of polymer surface modifications for various biomedical applications.

I am thankful to Prof. A.K. Ghosh, Prof. J. Jacob, Prof. B.K. Satapathy, Prof. Leena Nebhani, Prof. B. Tripathi and all faculties of DMSE, IIT Delhi, for their constant encouragement and help throughout my research work. I express my thanks to Prof. Neetu Singh, Department of Biochemical Engineering and Prof. Jayanta Bhattacharya IIT Delhi, for providing facilities to carry out experiments in their lab. It is a pleasure for me to express my gratitude towards all my labmates, an unbroken bond of friendship and brotherhood that prevails in the laboratory is due to the wonderful colleagues. Their warm affection, support during tough times, nice scientific interactions, involvement and conscious as well as unconscious help have rendered my research life a bountiful time. It was really fun to work in their association. I would like to thank all my seniors Dr. Shivangi Sharma, Dr. Agni Kumar Biswal, Dr. Sumbul Hafeez, Dr. Ifra, Dr. Sabapathy, Dr. Sucharita, Dr. Devendra Mogha, Shikha, Subhra my batchmates, Tina Joshi, Aanchal, Ajit, Anubhav, Ashok, Kalpana Pandey and juniors Shubhashree Pradhan, Abhishek Bhattacharya Saumyadip Dutta, Nidhi Gupta, Meenaskhi Verma, Aiswarya TT, Amit from IIT Delhi for their constant encouragement.

My special thanks to Mr. Surender Sharma, Mr. Shivkant, Mr. Ashok Kapoor, Mr. Islam, Mr. Gajraj, Mrs. Shalini Arora, Mr. Subhash, Amit, Pramod, and Sudhir Pandey, for their immediate help whenever needed. My family members deserve special attention for their support and persistent confidence in me, but I don't have words to express my gratitude for them. I am extraordinarily fortunate to have the blessings of my grandfather Late Mr. Ramnath Dhingra ji and Shri Tek Chand Bhalla, my grandmother Late Rajkumari ji, my Nani who is always with me Hukum Devi ji, my father M Prem Prakash Dhingra and my mother Mrs. Sunita Dhingra who always bless me every day with the shower of their love, providing inner strength, patience, emotional support and making sacrifices for my successful career. I express my heartiest thanks to my sister Barkha Dhingra and brother Shantanu Dhingra for his constant support, encouragement, and patience which enable me to pursue my career. Finally, I would like to thank everyone who helped me in the successful compilation of thesis, as well as expressing my apology that I could not mention personally one by one.

I would like to acknowledge the financial assistance received from MHRD which has helped me to pursue my Ph.D. without any stress.

Last but not the least I am thankful to the Almighty God in helping me to accomplish this task.

Shaifali Dhingra

ABSTRACT

Bacteria assisted infections on biomaterials used as implant/device are one of the major threats to human health. Microbial resistant coatings on biomaterials can potentially be considered to mitigate the biomaterial associated infections. Usually bio-materials with leachable antimicrobial coatings, though economically attractive, provide only short-term protection of the surface against bacteria. Therefore, a stable, non-fouling or bactericidal and biocompatible polymeric coating is highly desirable. In this regard, infection resistant polymer brushes, defined as polymer chains tethered to surface by one end, with suitable anti-infective functionality represent a useful class of non-leaching coatings. Generally, the brushes are covalently connected to the underlying surface, thus prolonging the infection resistant property of the coated surface. Surface initiated atom transfer radical polymerization (SI-ATRP) is a versatile technique for the generation of polymeric brushes via ‘grafting from’ way. This technique was used throughout the study for conjugating polymer brush to the underlying polyester substrate.

In order to accomplish the goal, we have synthesized and developed an infection resistant yet cytocompatible coating on actual biomaterials comprised of tartaric acid based biodegradable aliphatic polyester. In chapter 2 we have primarily focused on attaching anti-infective polymer brushes such as poly (2-hydroxyethyl methacrylate) (PHEMA), poly (poly (ethylene glycol) methacrylate) (PPEGMA) and poly[(2-methacryloyloxyethyl] trimethyl ammonium chloride) (PMETA) on hydroxyl functionalized polyester substrate via SIATRP. The brushes were thoroughly characterized for reaction kinetics, grafting yield, surface density, topography and hydrophilicity. Among the various brushes, cationic polymer brush (PMETA) was found to exhibit highest antibacterial activity, with only ~3% and ~4% adherence of *E. coli* (*Escherichia coli*) and *S. aureus* (*Staphylococcus aureus*), respectively. In order to show its widespread use and also to vary initiator density, polylactic acid (PLA) was blended with this tartaric acid based aliphatic polyester and a 3D (three-dimensional) scaffold was fabricated by 3D printing using the blend. Finally, PMETA brush was grown onto the scaffold surface for various time periods and the evaluation of antibacterial activity (using gram positive and gram-negative bacteria) and cytocompatibility (using mammalian osteoblast cells) were carried out on the brush modified scaffold. A balance between antibacterial activity and cytocompatibility was found at optimum brush length achieved after 18 h of SIATRP suggesting that this composition offers a stable, non-leaching, anti-infective, but cytocompatible coating on biodegradable polymeric implant surface for addressing several biomaterials associated

infections. The mechanistic understandings also provide insight into that cationic polymer brush grafted onto the tartaric acid based polymeric scaffold possess the highest antibacterial property amongst all the brushes with 50% cytocompatibility. Therefore, there was a need to combat the cytocompatibility issue.

In chapter 3 we have discussed about the formation of mixed brushes which were nothing but a combination of poly(3-dimethyl-(methacryloyloxyethyl) ammonium propane sulfonate) (polyDMAPS) and poly((oligo ethylene glycol) methyl ether methacrylate) (polyPEGMA) with varying chain length (n) of the ethylene glycol unit ($n = 1, 6, 11, \text{ and } 21$). Both homo and copolymeric brushes of polyDMAPS with polyPEGMA exhibited antibacterial efficacy against both Gram positive and Gram-negative pathogens such as *E. coli* (*Escherichia coli*) and *S. aureus* (*Staphylococcus aureus*) because of the combined action of bacteriostatic effects originating from strongly hydrated layers present in zwitterionic (polyDMAPS) and hydrophilic (polyPEGMA) copolymer brushes. Interestingly, a mixed polymer brush comprising polyDMAPS and polyPEGMA (ethylene glycol chain unit of 21) at 50/50 molar ratio provided zero bacterial growth and almost 100% cytocompatibility (tested using L929 mouse fibroblast cells), making the brush-modified biodegradable substrate an excellent choice for an infection-resistant and cytocompatible surface. An attempt was made to understand their extraordinary performance with the help of contact angle, surface charge analysis and nanoindentation study, which revealed the formation of a hydrophilic, almost neutral, very soft surface (99.99% reduction in hardness and modulus) after modification with the mixed brushes. This may completely suppress bacterial adhesion. Animal studies demonstrated that these brush-modified scaffolds are biocompatible and can mitigate wound infections. Overall, this study shows that the fascinating combination of an infection-resistant and cytocompatible surface can be generated on biodegradable polymeric surfaces by modulating the surface hardness, flexibility and hydrophilicity by selecting appropriate functionality of the copolymeric brushes grafted onto them, making them ideal non-leaching, anti-infective, haemocompatible and cytocompatible coatings for biodegradable implants.

In chapter 4, we have demonstrated the formation of polymer brush in spatio-selective domain created on biodegradable aliphatic polyester substrate to develop micropatterned cells, bacteria etc. on microtextured surfaces. Micropatterning biological entities is one of the most sought-after technologies for producing cell/bacteria microarrays, biochips, diagnostics, biosensors etc. In the current study, surface of tartaric acid based biodegradable aliphatic polyester was micropatterned using photochemistry with the help of a mask. Around 10% PAG (photoacid generator, 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5 triazine) was encapsulated in the

polyester matrix. Exposure of UV radiation on the matrix at 395 nm for 25 min triggered the acid release from unmasked area where ATRP (Atom Transfer Radical Polymerization) initiating moiety was immobilized onto hydroxyl functionality originated from acid triggered removal of isopropylidene groups from the polyester. In subsequent step, polyPEGMA (poly (ethylene glycol) methyl ether methacrylate) brushes of ~900 nm thick were allowed to grow from illuminated areas only. Similar process was repeated after removing the mask to grow ~770 nm thick zwitterionic polyDMAPS (poly(3-dimethyl- (methacryloyloxyethyl) ammonium propane sulfonate)), brush from previously masked domain only. Ultimately, an alternate pattern of polyPEGMA and polyDMAPS brushes (in the form of square) was generated on biodegradable polyester surface. Patterned surface modified with dual brushes was found to be antifouling in nature (rejection of >97% of proteins). Strikingly, an alternate pattern of live bacterial cell (*E. coli* and *S. Aureus*) was evident on the dual brush modified patterned surface and relatively higher population of bacteria was found on polyPEGMA brush modified domain. However, a complete reverse pattern was visible in case of L929 mouse fibroblast cells, i.e., cells were predominantly found to be adhered and proliferated along the region of zwitterionic brush modified surface as observed from SEM and fluorescent images. This innovative strategy employed on biodegradable polymer surface provides an easy and straightforward way to micropattern various biological macromolecules such as cells, bacteria etc. on biodegradable substrates which hold great potential to function as biochips having arrays of cell/bacteria/specific biomolecule etc.

In the next chapter 5, we have constructed a highly antibacterial as well as biocompatible mixed zwitterionic polymer brushes of different chain length onto the surface of 3D printed scaffold made of tartaric acid based aliphatic polyester blend for wound healing applications. The mixed zwitterionic polymer brushes were combination of poly(3-dimethyl-(methacryloyloxyethyl) ammonium propane sulfonate) and polysulfobetaine methacrylate with variable carbon chain length (n=6 and 12). Both homo and copolymeric brush of polyDMAPS and polysulfobetaine methacrylate along with different chain possessed antibacterial effectiveness against both gram positive and gram negative pathogens such as *E. coli* (*Escherichia coli*) and *S.aureus* (*Staphylococcus aureus*) because of conglomerate effect of bacteriostatic as well as bactericidal effect arising from strongly hydrated layers present in different carbon chain length of zwitterionic (polyDMAPS) hydrophilic copolymer brushes. Interestingly, mixed polymer brush with a combination polysulfobetaine methacrylate of chain length n= 6 and 12 at 50/50 ratio stipulated zero bacterial growth and well-nigh 100% cytocompatibility (tested using Hela cells) making the brush modified biodegradable substrate as a fantabulous selection for infection

resistant and Biocompatible surface. Animal studies demonstration proved that these brush-modified scaffold can hasten the wound repairs. Whole, this work shows that an enthralling combination of highly infection resistant and biocompatible surface can be produced onto biodegradable polymeric surface by tuning the surface roughness, and hydrophilicity by choosing suitable functionality of the chain variable copolymeric brushes grafted onto them, making them a perfect non-leaching, anti-infective, and biocompatible coatings for the devolution of infection resistant implants for wound healing applications without hampering the tissue compatibility.

Finally, in the last chapter, spatio-selective immobilization of dual metallic nanoparticles on binary polymer brushes grafted onto biodegradable polymeric surfaces was discussed. Generally, biodegradable polymers employed in the fabrication of biomedical and biosensing devices suffer from diversity, due to the absence of functional groups in such materials which do not allow the use of common surface chemistries to conjugate biomolecules on them. Herein we report the use of copolymer of tartaric acid-based polyester, and alkyne functionalized polylactic acid as underlying substrate to graft binary brushes such as Poly3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate (polyDMAPS, zwitterionic) and poly[(2-methacryloyloxyethyl) trimethyl ammonium chloride) (PMETA, cationic) in selective regions. Orthogonal chemistries such as exploitation of photochemistry and click chemistry were explored to immobilize initiators onto tartaric acid based polyester part and alkyne functionalized polylactide part by using mask to create micropatterned surface. Subsequently, binary brushes were grafted from the specific regions only. The surface modification and pattern stability were confirmed with fluorescence microscopy, Raman spectroscopy, EDX mapping, contact angle and X-ray photoelectron spectroscopy (XPS), showing an effective strategy to create patterned substrate. Ultimately, dual metal nanoparticles such as gold and silver were selectively immobilized on cationic and zwitterionic brushes, respectively via electrostatic interaction by altering pH of the dipping medium. The dual metal nanoparticles were then explored for immobilizing binary proteins or double stranded DNA onto selective areas, thereby forming an alternate pattern of two different proteins or double stranded DNA. In future, this type of hybrid protein patterned substrate can be a promising surface for multiplexed detection of DNA sequences.

सार

इम्प्लांट/डिवाइस के रूप में शरीर के अंदर उपयोग किए जाने वाले बायोमैटेरियल्स पर बैक्टीरिया से होने वाले संक्रमण मानव स्वास्थ्य के लिए प्रमुख खतरों में से एक हैं। बायोमैटेरियल्स पर माइक्रोबियल प्रतिरोधी कोटिंग्स को संभावित रूप से बायोमैटेरियल से जुड़े संक्रमणों को कम करने के लिए माना जा सकता है। आमतौर पर लीचेबल रोगाणुरोधी कोटिंग्स के साथ जैव सामग्री, हालांकि आर्थिक रूप से आकर्षक, बैक्टीरिया के खिलाफ सतह की केवल अल्पकालिक सुरक्षा प्रदान करती है। इसलिए, एक स्थिर, गैर-दूषण या जीवाणुनाशक और जैव-संगत बहुलक कोटिंग अत्यधिक वांछनीय है। इस संबंध में, बहुलक ब्रश, एक छोर से सतह पर बंधे बहुलक श्रृंखला के रूप में परिभाषित, उपयुक्त विरोधी संक्रामक कार्यक्षमता के साथ स्थिर कोटिंग्स के एक उपयोगी वर्ग का प्रतिनिधित्व करते हैं जो सहसंयोजक रूप से अंतर्निहित सतह से जुड़े होते हैं, इस प्रकार लेपित सतह के संक्रमण प्रतिरोध को लम्बा खींचते हैं। सरफेस इनिशिएटेड एटम ट्रांसफर रेडिकल पोलिमराइजेशन (एसआई-एटीआरपी) 'ग्राफिटिंग फ्रॉम' तरीके से पॉलीमेरिक ब्रश बनाने की एक बहुमुखी तकनीक है। लक्ष्य को प्राप्त करने के लिए, हमने टार्टरिक एसिड आधारित बायोडिग्रेडेबल एलीफैटिक पॉलिएस्टर से युक्त संक्रमण प्रतिरोधी अभी तक साइटोकम्पैटिबल बायोमैटेरियल्स को संश्लेषित और विकसित किया है, अध्याय 2 में हमने मुख्य रूप से पॉली (2-हाइड्रॉक्सीएथाइल मेथैक्रिलेट) जैसे एंटी-इन्फेक्टिव पॉलीमर ब्रश को जोड़ने पर ध्यान केंद्रित किया है। (PHEMA), पॉली (पॉली (एथिलीन ग्लाइकॉल) मेथैक्रिलेट) (PPEGMA) और पॉली [(2-मेथैक्रिलोयॉक्सीथाइल] ट्राइमेथाइल अमोनियम क्लोराइड) (PMETA) सतह के माध्यम से हाइड्रॉक्सिल फंक्शनल पॉलिएस्टर सबस्ट्रेट पर एटम ट्रांसफर रेडिकल पोलिमराइजेशन (SIATRP) शुरू किया। ब्रश को प्रतिक्रिया कैनेटीक्स, ग्राफिटिंग उपज, सतह घनत्व, स्थलाकृति और हाइड्रोफिलिसिटी के लिए पूरी तरह से चित्रित किया गया था। विभिन्न ब्रशों में, cationic बहुलक ब्रश (PMETA) को उच्चतम जीवाणुरोधी गतिविधि प्रदर्शित करने के लिए पाया गया, केवल ~ 3% और ~ 4% ई। कोलाई (एस्चेरिचिया कोलाई) और एस। ऑरियस (स्टैफिलोकोकस ऑरियस) के पालन के साथ। इसके व्यापक उपयोग को दिखाने के लिए और सर्जक घनत्व को बदलने के लिए, पॉलीएलैक्टिक एसिड (पीएलए) को इस टार्टरिक एसिड आधारित एलीफैटिक पॉलिएस्टर के साथ मिश्रित किया गया था और मिश्रण का उपयोग करके 3 डी प्रिंटिंग द्वारा एक 3 डी (तीन-आयामी) मचान तैयार किया गया था। अंत में, पीएमईटीए ब्रश को विभिन्न समय अवधि के लिए मचान की सतह पर उगाया गया और ब्रश संशोधित

मचान पर जीवाणुरोधी गतिविधि (ग्राम पॉजिटिव और ग्राम-नेगेटिव बैक्टीरिया का उपयोग करके) और साइटोकम्पैटिबिलिटी (स्तनधारी ऑस्टियोब्लास्ट कोशिकाओं का उपयोग करके) का मूल्यांकन किया गया। SIATRP के 18 घंटे के बाद प्राप्त इष्टतम ब्रश लंबाई पर जीवाणुरोधी गतिविधि और साइटोकम्पैटिबिलिटी के बीच एक संतुलन पाया गया था, यह सुझाव देता है कि यह संरचना कई बायोमैटिरियल्स से जुड़े संक्रमणों को संबोधित करने के लिए बायोडिग्रेडेबल पॉलीमरिक इम्प्लांट सतह पर एक स्थिर, गैर-लीचिंग, एंटी-संक्रमण, लेकिन साइटोकंपैटिबल कोटिंग प्रदान करती है। यंत्रवत समझ भी टैटरिक एसिड आधारित पॉलीमरिक स्कैफोल्ड पर ग्राफ्ट किए गए उस cationic बहुलक ब्रश में अंतर्दृष्टि प्रदान करती है, जिसमें 50% साइटोकम्पैटिबिलिटी के साथ सभी ब्रशों में सबसे अधिक जीवाणुरोधी गुण होते हैं। इसलिए साइटोकम्पैटिबिलिटी मुद्दे का मुकाबला करने की आवश्यकता थी। अध्याय 3 में मिश्रित ब्रश और कुछ नहीं बल्कि पॉली(3-डाइमिथाइल- (मेथैक्रिलोयॉक्सीथाइल) अमोनियम प्रोपेन सल्फोनेट) (पॉलीडीएमएपीएस) और पॉली ((ओलिगो एथिलीन ग्लाइकॉल) मिथाइल ईथर मेथैक्रिलेट) (पॉलीपीईजीएमए) के संयोजन के अलावा अलग-अलग श्रृंखला लंबाई (एन) के संयोजन थे। एथिलीन ग्लाइकोल इकाई (एन = 1, 6, 11, और 21) की। पॉलीपीईजीएमए के साथ पॉलीडीएमएपीएस के दोनों होमो और कोपोलिमरिक ब्रश ने ग्राम पॉजिटिव और ग्राम नेगेटिव रोगजनकों जैसे ई। कोलाई (एस्चेरिचिया कोलाई) और एस। ऑरियस (स्टैफिलोकोकस ऑरियस) दोनों के खिलाफ जीवाणुरोधी प्रभावकारिता का प्रदर्शन किया क्योंकि दृढ़ता से हाइड्रेटेड परतों से उत्पन्न होने वाले बैक्टीरियोस्टेटिक प्रभावों की संयुक्त कार्रवाई के कारण ज्वटरियोनिक (पॉलीडीएमएपीएस) और हाइड्रोफिलिक (पॉलीपीईजीएमए) कॉपोलीमर ब्रश में मौजूद है। दिलचस्प बात यह है कि 50/50 के अनुपात में पॉलीडीएमएपीएस और पॉलीपीईजीएमए (21 की एथिलीन ग्लाइकॉल चैन यूनिट) से युक्त एक मिश्रित पॉलीमर ब्रश ने शून्य जीवाणु वृद्धि और लगभग 100% साइटोकम्पैटिबिलिटी प्रदान की (L929 माउस फाइब्रोब्लास्ट कोशिकाओं का उपयोग करके परीक्षण किया गया), जिससे ब्रश-संशोधित बायोडिग्रेडेबल सबस्ट्रेट एक उत्कृष्ट बन गया। एक संक्रमण प्रतिरोधी और साइटोकम्पैटिबल सतह के लिए विकल्पा संपर्क कोण, सतह आवेश विश्लेषण और नैनोइंडेंटेशन अध्ययन की मदद से उनके असाधारण प्रदर्शन को समझने का प्रयास किया गया, जिसमें संशोधन के बाद एक हाइड्रोफिलिक, लगभग तटस्थ, बहुत नरम सतह (कठोरता और मापांक में 99.99% कमी) के गठन का पता चला। मिश्रित ब्रश। यह बैक्टीरिया के आसंजन को पूरी तरह से दबा सकता है। पशु अध्ययनों से पता चला है कि ये ब्रश-संशोधित मचान जैव-

संगत हैं और घाव के संक्रमण को कम कर सकते हैं। कुल मिलाकर, इस अध्ययन से पता चलता है कि एक संक्रमण-प्रतिरोधी और साइटोकंपैटिबल सतह का आकर्षक संयोजन बायोडिग्रेडेबल पॉलीमेरिक सतहों पर उत्पन्न किया जा सकता है, जो उन पर ग्राफ्ट किए गए कोपोलिमेरिक ब्रश की उपयुक्त कार्यक्षमता का चयन करके सतह की कठोरता, लचीलेपन और हाइड्रोफिलिसिटी को संशोधित करके, उन्हें आदर्श गैर-बायोडिग्रेडेबल इम्प्लांट्स के लिए लीचिंग, एंटी-इनफेक्टिव, हेमोकंपैटिबल और साइटोकंपैटिबल कोटिंग्स।

अध्याय 4 में इस काम में हमने घाव भरने वाले अनुप्रयोगों के लिए टार्टरिक एसिड आधारित एलिफैटिक पॉलिएस्टर मिश्रण से बने 3डी प्रिंटेड मचान की सतह पर विभिन्न श्रृंखला लंबाई ब्रशों के अत्यधिक जीवाणुरोधी के साथ-साथ जैव-संगत मिश्रित ज़िवटरियोनिक बहुलक बनाने के लिए एक कार्य योजना की सूचना दी है। मिश्रित ज़िवटरियोनिक पॉलीमर ब्रश पॉली (3-डाइमिथाइल- (मेथैक्रिलोयॉक्सिथाइल) अमोनियम प्रोपेन सल्फोनेट) और पॉलीसल्फोबेटाइन मेथैक्रिलेट के साथ चर कार्बन श्रृंखला लंबाई (एन = 6 और 12) के संयोजन थे। पॉलीडीएमएपीएस और पॉलीसल्फोबेटाइन मेथैक्रिलेट के होमो और कोपोलिमेरिक ब्रश दोनों के साथ-साथ विभिन्न श्रृंखलाओं में ग्राम पॉजिटिव और ग्राम नकारात्मक रोगजनकों जैसे ई। कोलाई (एस्चेरिचिया कोलाई) और एस.ऑरियस (स्टैफिलोकोकस ऑरियस) दोनों के खिलाफ जीवाणुरोधी प्रभाव होता है, क्योंकि बैक्टीरियोस्टैटिक के समूह प्रभाव के कारण भी। ज़िवटरियोनिक (पॉलीडीएमएपीएस) हाइड्रोफिलिक कॉपोलीमर ब्रश की विभिन्न कार्बन कैन लंबाई में मौजूद दृढ़ता से हाइड्रेटेड परतों से उत्पन्न जीवाणुनाशक प्रभाव के रूप में। दिलचस्प बात यह है कि 50/50 अनुपात में श्रृंखला लंबाई $n = 6$ और 12 के संयोजन पॉलीसल्फोबेटाइन मेथैक्रिलेट के साथ मिश्रित बहुलक ब्रश ने शून्य जीवाणु विकास और अच्छी तरह से 100% साइटोकंपैटिबिलिटी (हेला कोशिकाओं का उपयोग करके परीक्षण) निर्धारित किया, जिससे ब्रश को एक शानदार चयन के रूप में बायोडिग्रेडेबल सबस्ट्रेट को संशोधित किया गया। संक्रमण प्रतिरोधी और जैव-संगत सतह के लिए। पशु अध्ययन प्रदर्शन ने साबित कर दिया कि ये ब्रश-संशोधित मचान घाव की मरम्मत में तेजी ला सकते हैं। कुल मिलाकर, यह काम दिखाता है कि अत्यधिक संक्रमण प्रतिरोधी और जैव-संगत सतह का एक आकर्षक संयोजन सतह खुरदरापन को ट्यून करके बायोडिग्रेडेबल पॉलीमेरिक सतह पर उत्पादित किया जा सकता है, और हाइड्रोफिलिसिटी श्रृंखला परिवर्तनीय कोपोलिमेरिक ब्रश की उपयुक्त कार्यक्षमता चुनकर उन पर ग्राफ्ट किया जा सकता है, जिससे उन्हें एक आदर्श गैर बना दिया जा सकता है। उक्तक अनुकूलता में बाधा डाले बिना घाव भरने वाले अनुप्रयोगों के लिए संक्रमण प्रतिरोधी

प्रत्यारोपण के हस्तांतरण के लिए लीचिंग, संक्रमण-रोधी और जैव-संगत कोटिंग्स। पिछले अध्याय में हमने सूक्ष्म बनावट वाली सतहों पर कोशिकाओं, बैक्टीरिया आदि के माइक्रोपैटर्निंग के बारे में चर्चा की है, जो सेल / बैक्टीरिया माइक्रोएरे, बायोचिप्स, डायग्नोस्टिक्स, बायोसेंसर आदि के उत्पादन के लिए सबसे अधिक मांग वाली तकनीक में से एक है। वर्तमान अध्ययन में, टार्टरिक एसिड की सतह आधारित बायोडिग्रेडेबल एलीफैटिक पॉलिएस्टर को मास्क की मदद से फोटोकैमिस्ट्री का उपयोग करके माइक्रोपैटर्न किया गया था। पॉलिएस्टर मैट्रिक्स में लगभग 10% पीएजी (फोटोएसिड जनरेटर, 2-(4-मेथॉक्सीस्टीरिल) -4,6-बीआईएस (ट्राइक्लोरोमेथाइल) -1,3,5 ट्राईजिन) को एनकैप्सुलेट किया गया था। मैट्रिक्स पर यूवी विकिरण के 25 मिनट के लिए 395 एनएम पर एक्सपोजर ने अनमास्क क्षेत्र से एसिड रिलीज को ट्रिगर किया जहां एटीआरपी (एटम ट्रांसफर रेडिकल पॉलीमराइजेशन) की शुरुआत करने वाले हाइड्रॉक्सिल कार्यक्षमता पर स्थिर हो गए थे, जो पॉलिएस्टर से आइसोप्रोपाइलिडीन समूहों के एसिड ट्रिगर हटाने से उत्पन्न हुआ था। बाद के चरण में, ~ 900 एनएम मोटे पॉलीपीईजीएमए (पॉली (एथिलीन ग्लाइकॉल) मिथाइल ईथर मेथैक्रिलेट) ब्रश को केवल प्रबुद्ध क्षेत्रों से बढ़ने दिया गया। ~ 770 एनएम मोटी zwitterionic polyDMAPS (पॉली (3-डाइमिथाइल- (मेथैक्रिलोयॉक्सीथाइल) अमोनियम प्रोपेन सल्फोनेट)) बढ़ने के लिए मास्क को हटाने के बाद इसी तरह की प्रक्रिया को दोहराया गया था, केवल पहले से नकाबपोश डोमेन से ब्रश। अंततः, पॉलीपेग्मा और पॉलीडीएमएपीएस ब्रश (वर्ग के रूप में) का एक वैकल्पिक पैटर्न बायोडिग्रेडेबल पॉलिएस्टर सतह पर उत्पन्न हुआ था। दोहरे ब्रशों के साथ संशोधित प्रतिरूपित सतह प्रकृति में एंटीफिलिंग (> 97% प्रोटीन की अस्वीकृति) पाई गई। आश्चर्यजनक रूप से, जीवित जीवाणु कोशिका (ई। कोलाई और एस। ऑरियस) का एक वैकल्पिक पैटर्न दोहरे ब्रश संशोधित पैटर्न वाली सतह पर स्पष्ट था और पॉलीपेग्मा ब्रश संशोधित डोमेन पर बैक्टीरिया की अपेक्षाकृत अधिक आबादी पाई गई थी। हालाँकि, L929 माउस फ़ाइब्रोब्लास्ट कोशिकाओं के मामले में एक पूर्ण रिवर्स पैटर्न दिखाई दे रहा था, अर्थात्, कोशिकाओं को मुख्य रूप से पालन किया गया था और zwitterionic ब्रश संशोधित सतह के क्षेत्र के साथ प्रसार किया गया था जैसा कि SEM और फ्लोरोसेंट छवियों से देखा गया था। बायोडिग्रेडेबल पॉलीमर सतह पर नियोजित यह अभिनव रणनीति बायोडिग्रेडेबल सबस्ट्रेट्स पर विभिन्न जैविक मैक्रोमोलेक्यूल्स जैसे सेल, बैक्टीरिया आदि को माइक्रोपैटर्न करने का एक आसान और सीधा तरीका प्रदान करती है, जो बायोचिप्स के रूप में सेल/बैक्टीरिया/विशिष्ट बायोमोलेक्यूल्स आदि के सरणियों के रूप में कार्य करने की बड़ी क्षमता रखते हैं।

अंत में अंतिम अध्याय में बायोमेडिकल और बायोसेंसिंग उपकरणों के निर्माण में नियोजित बायोडिग्रेडेबल पॉलीमेरिक सतहों पर ग्राफ्ट किए गए बाइनरी पॉलीमर ब्रश पर दोहरे धातु नैनोकणों का अनुपात-चयनात्मक स्थिरीकरण आम तौर पर एक चुनौतीपूर्ण मुद्दा है, क्योंकि ऐसी सामग्रियों में कार्यात्मक समूहों की अनुपस्थिति अनुमति नहीं देती है। सामान्य सतह रसायन विज्ञान का उपयोग। इसमें हम टैटरिक एसिड-आधारित पॉलिएस्टर के कॉपोलीमर के उपयोग की रिपोर्ट करते हैं, और एल्काइन फंक्शनल पॉलीलैक्टिक एसिड को बाइनरी ब्रश जैसे पॉली 3-डाइमिथाइल- (मेथैक्रिलोयॉक्सीथाइल) अमोनियम प्रोपेन सल्फोनेट (पॉलीडीएमएपीएस, ज़्विटरियोनिक) और पॉली [(2-मेथैक्रिलोयॉक्सिथाइल) को ग्राफ्ट करने के लिए अंतर्निहित सबस्ट्रेट के रूप में उपयोग करते हैं] ट्राइमेथिल अमोनियम क्लोराइड) (PMETA, cationic) चुनिंदा क्षेत्रों में। फोटोकैमिस्ट्री और क्लिक केमिस्ट्री के शोषण जैसे ऑर्थोगोनल केमिस्ट्री को माइक्रोपैटर्न वाली सतह बनाने के लिए मास्क का उपयोग करके टैटरिक एसिड आधारित पॉलिएस्टर भाग और एल्काइन फंक्शनल पॉलीएक्टाइड भाग पर सर्जक को स्थिर करने के लिए खोजा गया था। इसके बाद, बाइनरी ब्रश केवल विशिष्ट क्षेत्रों से ही ग्राफ्ट किए गए थे। सतह संशोधन और पैटर्न स्थिरता की पुष्टि फ्लोरेसेंस माइक्रोस्कोपी, रमन स्पेक्ट्रोस्कोपी, ईडीएक्स मैपिंग, संपर्क कोण और एक्स-रे फोटोइलेक्ट्रॉन स्पेक्ट्रोस्कोपी (एक्सपीएस) के साथ की गई थी, जो पैटेरेड सबस्ट्रेट बनाने के लिए एक प्रभावी रणनीति दिखाती है। अंततः, सोने और चांदी जैसे दोहरे धातु के नैनोकणों को चुनिंदा रूप से cationic और zwitterionic ब्रश पर स्थिर किया गया, क्रमशः इलेक्ट्रोस्टैटिक इंटरैक्शन के माध्यम से सूई माध्यम के पीएच को बदलकर। दोहरे धातु के नैनोकणों को तब द्विआधारी प्रोटीन को चयनात्मक क्षेत्रों पर स्थिर करने के लिए खोजा गया था, जिससे दो अलग-अलग प्रोटीनों का एक वैकल्पिक पैटर्न बन गया। भविष्य में, इस प्रकार का हाइब्रिड प्रोटीन पैटर्न वाला सबस्ट्रेट डीएनए अनुक्रमों के बहुसंकेतन का पता लगाने के लिए एक आशाजनक सतह हो सकता है।

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LIST OF ABBREVIATIONS

| List of abbreviations | Full form |
|------------------------------|---|
| WHO | World Health Organization |
| SSI | surgical site infections |
| SIATRP | surface-initiated atom transfer polymerization mediated |
| c-PMMA | carboxy terminated polymethyl methacrylate |
| QAS | quaternary ammonium salt |
| ROMP | ring-opening metathesis polymerization |
| RAFT | reversible addition–fragmentation transfer |
| NMP | nitroxide-mediated polymerization |
| RGD | arginine-glycine-aspartic |
| MIC | minimum inhibitory concentration |
| CMC | Carboxymethyl Cellulose |
| SLIPS | Slippery liquid-infused porous surface |
| (PDMS-OCH ₃) | polydimethylsiloxane |
| CST | Critical Solution Temperature |
| AMP | antimicrobial peptides |
| HA-GS | hydroxyapatite and gentamicin sulphate |
| ACLs | quaternized with different alkyl halides |
| P-PQAs | quaternary ammonium salt based polyacrylates |
| Tet213 (KRWWKWRRC) | Cysteine-functionalized cationic antimicrobial peptide |
| SI-PIMP | surface-initiated photoiniferter mediated polymerization |
| BMSC's | bone marrow mesenchymal cells |
| (CP-PC) | Phosphate-Choline interactions |
| (SNMs) | silicon nanopore membranes |
| TC-PDVBAPS | triclosan immobilized polyDVBAPS brushes |
| ITO | indium tin oxide |
| APTT | Activated partial thromboplastin time |

| | |
|-------------|---|
| (HT1080) | human fibroblast |
| PLA | Poly(lactic acid) |
| PMDETA | Pentamethyl Diethylene Tetraacetate |
| polyDMAPS | poly(3-dimethyl-(methacryloyloxyethyl) ammonium propane sulfonate) |
| EDTA | Ethylene Diamine Tetraacetate |
| polyPEGMA | poly((oligo ethylene glycol) methyl ether methacrylate) |
| THF | Tetrahydrofuran |
| PHEMA | poly (2-hydroxyethyl methacrylate) |
| PMETA | poly[(2-methacryloyloxyethyl] trimethyl ammonium chloride) |
| (DCM) | dichloromethane |
| (E. coli) | Escherichia coli |
| (S. aureus) | Staphylococcus aureus |
| (MG-63) | mammalian osteoblast cells |
| (LB) | Luria broth |
| MTT | (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide) |
| BPY | 2,2'-bipyridine |
| (BIBB) | 2-bromoisobutyryl bromide |
| BSA | Bovine Serum Albumin |
| (SCFS) | Single-cell force spectroscopy |
| FESEM | Field Emission Scanning Electron Microscopic |
| SEM | Scanning electron microscope |
| FTIR | Fourier Transform Infrared Spectroscopy |
| TGA | Thermal Gravimetric Analysis |
| GPC | Gel Permeation Chromatography |
| NMR | Nuclear Magnetic Resonance |
| ATR-FTIR | Attenuated Total Reflectance-Fourier Transform Infrared |
| DSC | Differential Scanning Calorimetry |

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| XPS | X-ray photoelectron spectroscopy |
| OM | Optical Microscopy |
| AFM | Atomic Force Microscopy |
| EDX | Energy Dispersive X-ray |