

**AMINE FUNCTIONALIZED POROUS POLYMERIC
MATERIALS FOR HETEROGENOUS CATALYSIS AND
ANTIMICROBIAL APPLICATION**

AMIT KUMAR



**DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY**

JUNE 2024

© Indian Institute of Technology Delhi (IITD), New Delhi, 2024

**AMINE FUNCTIONALIZED POROUS POLYMERIC
MATERIALS FOR HETEROGENOUS CATALYSIS AND
ANTIMICROBIAL APPLICATION**

by

Amit Kumar

Department of Materials Science and Engineering

Submitted

in fulfilment of the requirements of the degree of

Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY

JUNE 2024

dedicated to my Family

CERTIFICATE

This is to certify that the thesis entitled " **Amine Functionalized Porous Polymeric Materials for Heterogenous Catalysis and Antimicrobial Application**" being submitted by Mr. Amit Kumar to the Indian Institute of Technology Delhi for the award of the degree of Doctor of Philosophy, is a record of bonafide research work carried out by him.

Prof. Leena Nebhani

Associate Professor

Department of Materials Science & Engineering

Indian Institute of Technology Delhi

Hauz Khas, New Delhi - 110016

ACKNOWLEDGEMENTS

I would like to begin by extending my heartfelt thanks to my thesis advisor, Professor Leena Nebhani. I am indebted to her for the guidance and opportunities which will help me throughout my career. She has always encouraged me to develop a deep understanding and carry out meaningful scientific research. Additionally, I wish to express my appreciation to the members of the SRC, including Prof. Josemon Jacob, Saha, and Preeti Srivastava, for their invaluable suggestions and feedback throughout the process. I would like to express my gratitude to Prof. Dirk Kuckling from University of Paderborn in Germany for hosting me in his lab for three months under the DST-DAAD program. I am highly thankful to Prof. R. K. Shukla and Prof. Prashant Tevatia for personally teaching me several experimental techniques. It is my pleasure to thank Mr. E. Islam, Mr. Surendra, Mr. Gajraj, Mrs. Astha, Mr. Jitendra, Mr. Brijesh, and Mr. Gyanendra, Mrs. Shalini, Mr. Amit, Mr. Sudhir, Mr. Narendra, Mr. Aashish, Mr. Mohit, Mr. Rajesh, Mr. E. Islam, Mr. Shubham, Mr. Ramesh for tremendous support. I extend my sincere thanks to all the colleagues in Surface and Macromolecular Chemistry Laboratory and friends – Dr. Pratibha Sharma, Dr. Sumbul, Dr. Aanchal, Dr. Tina, E. Islam, Lukkumanul, Subhendu, Amit, Deepali, Gaurav, Ingita, Manish, Priyanshi, Rafiq, Subhajit, Debjit, Siddhesh, Reshma, Premchand, Abhishek, Hemant, Anubhav, Shailendra. I especially thank Dr. Pratibha Sharma for stimulating academic and non-academic discussions.

During my doctoral studies, I want to thank my all friends, for their support and help. Their presence has made this time genuinely memorable. I greatly acknowledge the generous financial support from the MHRD for my doctoral studies.

Expressing my sincerest gratitude to my family for their unwavering support and love – my parents, Mrs. Jaimala Devi and Mr. Vijay Pal Singh; My uncle, Mr. Raj Pal Singh; my sisters, Madhu, Sonika, Nisha and Vinti; my brother Dr. Pawan Kumar and late Sumit Kumar; my brother-in-law Mr. Dinesh Kumar and Mr. Ashish Chauhan; and my nephews Kartik, Raghav, Himank, and Yugank. Their love and constant belief in me give me the strength to face challenges with utmost courage. I am always indebted to them for their continuous encouragement and tireless efforts, which have been indispensable to my success.

Amit Kumar

ABSTRACT

This thesis presents a detailed investigation into the design, synthesis, and utilization of functional porous polymeric microparticles and macroporous antimicrobial polymer gels, aimed at addressing key challenges in catalysis and antimicrobial applications. Firstly, porous and nonporous microparticles via distillation-precipitation polymerization has been done, wherein varying contents of amine functionality are incorporated. These microparticles serve as catalysts for the Knoevenagel condensation reaction between 4-nitrobenzaldehyde and malononitrile. Porous microparticles exhibit superior catalytic activity, achieving complete conversion in ethanol at 50°C, owing to their larger accessible surface area. The proposed mechanism is determined by using density functional theory, elucidating the role of basic nitrogen sites in catalysis. Further, the fabrication of macroporous antimicrobial polymer gels (MAPGs) functionalized with quaternary ammonium cations of varying hydrocarbon chain lengths has been done using cryogelation. Antimicrobial activity, as well as the mechanical properties of the macroporous gels, was found to be influenced by the alkyl chain length attached to the quaternary ammonium cations as well as by the amount of crosslinker used for the fabrication of the gel. The gels based on the quaternized C8 monomer displayed the highest antimicrobial activity and mechanical stability as compared to the gels based on the C4 and C6 monomers. The escalation in antimicrobial performance with increasing hydrophobic alkyl chain has been attributed to enhanced hydrophobic interactions with bacterial cell walls. Furthermore, porous and nonporous microparticles functionalized with quinuclidine were synthesized for catalyzing the Baylis–Hillman reaction. Porous microparticles exhibited exceptional catalytic efficiency, achieving full conversion within 16 hours at 50 °C. The optimized system demonstrated promising recyclability over multiple cycles, underscoring its potential for sustainable catalytic processes. In addition, the synthesis of macroporous antimicrobial polymer gels incorporating quaternized quinuclidine with varying alkyl chain lengths has been done. Enhanced antimicrobial activity has been observed with longer alkyl chains, validated by molecular dynamics simulations elucidating the interaction with bacterial membranes. Additionally, the synthesis of porous microparticles immobilized with DMAP for catalyzing the Baylis–Hillman reaction has been done, which was optimized using DFT calculations to determine the energetics of reaction pathways. The catalyst's

reusability and efficiency across various reactants have been evaluated, offering insights into reaction kinetics and mechanisms. Lastly, smart solvent-responsive polymer gels functionalized with quaternized DMAP varying in alkyl chain length with inherent antimicrobial properties are designed and fabricated. Extensive characterization studies employing FTIR, and solid-state NMR provide insights into gel properties. Molecular dynamics simulations further elucidate gel interactions with bacterial membranes, contributing to a comprehensive understanding of their antimicrobial efficacy.

सारांश

यह थीसिस संवादात्मक गुंजाइश, संश्लेषण, और कार्यात्मक धारावाहिक पॉलीमरिक माइक्रोधातु और मैक्रोपोरस एंटीमाइक्रोबियल पॉलिमर जेल के डिज़ाइन, सिंथेसिस, और उपयोग का विस्तृत अध्ययन प्रस्तुत करती है, जो कैटलिसिस और एंटीमाइक्रोबियल अनुप्रयोगों में मुख्य चुनौतियों का समाधान करने का उद्देश्य रखती है। पहले, डिस्टिलेशन-निपटान पॉलिमरीकरण के माध्यम से धातुरीय और अधातुरीय माइक्रोधातु बनाए गए हैं, जिसमें अमाइन कार्यक्षमता की विभिन्न सामग्रियों को शामिल किया गया है। ये माइक्रोधातु नोएवेनगेल आंतरदीप्ति अभिक्रिया के लिए कैटलिस्ट के रूप में काम करते हैं, जो 4-नाइट्रोबेंजिल्डिहाइड और मैलोनोनाइट्राइल के बीच क्नोवेनागल आंतरदीप्ति अभिक्रिया है। धातुरीय माइक्रोधातु बड़े पृष्ठ क्षेत्र के कारण 50 °C पर एथेनॉल में पूर्ण परिवर्तन प्राप्त करते हैं, इसके लिए उन्होंने उत्तम कैटलिटिक गतिविधि प्रकट की है। प्रस्तावित अभिक्रिया मेकेनिक कार्य गणनाओं द्वारा पुष्टि की गई है, जो कैटलिसिस में बेसिक नाइट्रोजन साइटों की भूमिका को स्पष्ट करती है। और भी, क्रायोजेलेशन का उपयोग करके विभिन्न हाइड्रोकार्बन श्रृंग लंबाई के क्वाटर्नरी एमोनियम कैशन्स के साथ संयुक्त मैक्रोपोरस एंटीमाइक्रोबियल पॉलिमर जेल का निर्माण किया गया है। एंटीमाइक्रोबियल गतिविधि के साथ-साथ मैक्रोपोरस जेलों की मेकेनिकल गुणवत्ता को भी क्वाटर्नरी एमोनियम कैशन्स के संलग्न लंबाई के द्वारा प्रभावित पाया गया है और जेल के निर्माण के लिए क्रॉसलिंग के प्रयोग से। C8 मोनोमर पर आधारित जेल्स उच्चतम एंटीमाइक्रोबियल गतिविधि और यांत्रिक स्थिरता प्रदर्शित करते हैं जो C4 और C6 मोनोमर पर आधारित जेल्स के तुलना में होते हैं। एल्काइल श्रृंग की बढ़ती स्थिति में एंटीमाइक्रोबियल गतिविधि में उन्नति को बढ़ावा दिया गया है जो जीवाणु कोशिकाओं के अपने भारी अंश के साथ वृष्टि संवादों के साथ सुधारित अभिक्रियाओं का स्वागत करता है।

इसके अतिरिक्त, क्रिन्युक्लिडिन के साथ संयुक्त धातुरी और अधातुरी माइक्रोधातु बेरुनग्यक को बेरुनग्यक अभिक्रिया के लिए संशोधित किया गया। धातुरीय माइक्रोधातु अद्वितीय कैटलिटिक कुशलता प्रदर्शित करते हैं, 50 °C पर 16 घंटों में पूर्ण परिवर्तन प्राप्त करके अत्यधिक कैटलिटिक प्रभाव प्रदर्शित करते हैं। अनुकूलित प्रणाली बहुमुखी चक्रों पर अच्छे परिणाम प्रदर्शित करती है, जिससे इसकी स्थायी कैटलिटिक प्रक्रियाओं के लिए संभावनात्मकता को प्रमुखता दी जाती है। साथ ही, विभिन्न अल्काइल श्रृंग लंबाई के साथ क्वाटर्नरी विभिन्न हाइड्रोकार्बन श्रृंग के साथ संयुक्त मैक्रोपोरस एंटीमाइक्रोबियल पॉलिमर जेल का सिंथेसिस किया गया है। लंबे अल्काइल श्रृंग के साथ उन्नत एंटीमाइक्रोबियल गतिविधि को देखा गया है, जिसे जीवाणु मेम्ब्रेन के साथ अंतर्क्रिया को स्पष्ट करने वाले मोलेक्युलर गतिविधियों के द्वारा सत्यापित किया गया है।

इसके अतिरिक्त, कैटलाइजिंग बेलिस-हिलमैन अभिक्रिया के लिए डीएमएपी के साथ संशोधित पोरस माइक्रोधातुओं का संश्लेषण किया गया है, जिसे रिएक्शन पथ की ऊर्जा वायुमान का निर्धारण करने के लिए डीएफटी गणनाओं का उपयोग करके अनुकूलित किया गया था। कैटलिस्ट की पुनःप्रयोगिता और प्रभावशीलता को विभिन्न अभिक्रियाओं के साथ मूल्यांकित किया गया है, जो प्रतिक्रिया की गतिकी और तंत्रिकों में दर्शाते हैं। अंत में, बुद्धिमान रोग संवेदनशील पॉलिमर जेल डिज़ाइन और निर्माण किए गए हैं, जो अंतर्निहित एंटीमाइक्रोबियल गुणों के साथ अल्काइल श्रृंग लंबाई में विभिन्नता दिखाते हैं। जेल के गुणों के बारे में जानकारी प्रदान करने के लिए एफटीआईआर और ठोस-राज्य एनएमआर का उपयोग करने वाले व्यापक विश्लेषण अध्ययन किए गए हैं। अणुज गतिविधियों के सिमुलेशन ने जेल के जीवाणु मेम्ब्रेन के साथ अंतर्क्रिया को स्पष्ट किया है, जिससे उनकी एंटीमाइक्रोबियल प्रभावक्षमता के समग्र ज्ञान को संबोधित किया गया है।

TABLE OF CONTENT

CERTIFICATE	iii
ACKNOWLEDGEMENTS	iv
ABSTRACT	v
TABLE OF CONTENT	ix
LIST OF FIGURES	xiv
LIST OF ABBREVIATION	xxvi
Chapter 1. Introduction and Literature Review	1
1.1. Porous polymeric materials.....	2
1.2. Porous polymeric materials for heterogeneous catalysis.....	4
1.2.1. Porous polymer microparticles	6
1.2.2. Porous polymer microparticles as heterogeneous catalyst.....	9
1.2.3. Amine moieties as catalytic site	11
1.3. Polymer gels	15
1.3.1. Macroporous polymer gels	17
1.3.2. Macroporous antimicrobial polymer gels	23
1.3.3. Quaternary ammonium Compound as an antimicrobial agent	26
1.4. Literature Gap and Work Objective	28
1.5. Thesis Organization.....	29
1.6. References	31
Chapter 2(A). <i>N, N</i>-(Dimethylamino)ethyl methacrylate based porous polymer microparticles for catalyzing the Knoevenagel condensation reaction.....	37
2(A).1. Introduction	38
2(A).2. Experimental	40

2(A).2.1. Materials.....	40
2(A).2.2. Synthesis of porous poly(DMAEMA-co-DVB) microparticles.....	40
2(A).2.3. Synthesis of non-porous poly(DMAEMA-co-DVB) microparticles.....	41
2(A).2.4. Procedure for evaluating catalytic effect of microparticles towards Knoevenagel condensation.....	41
2(A).2.5. Procedure for the Synthesis of a Variety of Knoevenagel Products	42
2(A).2.6. Computational Method	44
2(A).2.7. Characterization Techniques	45
2(A).3. Results and Discussion.....	46
2(A).3.1. Characterization of microparticles	46
2A.3.2. Catalytic studies	52
2A.3.3. Recyclability of Microparticles for Catalysis.....	69
2(A).4. Conclusion.....	69
2(A).5. References.....	70

**Chapter 2(B). Fabrication of mechanically robust and highly bactericidal
macroporous polymeric gels based on quaternized *N*, *N*-(dimethylamino)ethyl
methacrylate possessing varying alkyl chain lengths.....73**

2(B).1. Introduction.	74
2(B).2. Experimental.....	75
2(B).2.1. Materials.....	75
2(B).2.2. Synthesis of quaternary ammonium (QA) monomers.....	75
2(B).2.3. Fabrication of macroporous antimicrobial polymeric gel.....	76
2(B).2.4. Swelling studies on MAPG.....	77
2(B).2.5. Antimicrobial assay	78
2(B).2.6. Flow cytometry experiment.....	78
2(B).2.7. Confocal microscopy.....	79

2(B).2.8. Characterization methods	79
2(B).2.9. Statistical analysis	81
2(B).3. Results and Discussion	81
2(B).4. Conclusion.	108
2(B).5. References	109
Chapter 3(A). Quinuclidine based porous polymer microparticles for catalyzing the Baylis-Hillman reaction.....	112
3(A).1. Introduction	113
3(A).2. Experimental.....	115
3(A).2.1. Materials.....	115
3(A).2.2. Synthesis of quinuclidin-3-yl methacrylate (QM)	115
3(A).2.3. Synthesis of non-porous poly (QM-co-DVB) microparticles.....	115
3(A).2.4. Synthesis of porous poly (QM-co-DVB) microparticles.	116
3(A).2.5. Procedure for evaluating the catalytic effect of microparticles towards Baylis-Hillman reaction.	117
3(A).2.6. Procedure for the synthesis of variety of Baylis-Hillman products.....	117
3(A).2.6. Characterization	119
3(A).3. Results and Discussion.....	120
3(A).4. Conclusion.	141
3(A).5. References	142
Chapter 3(B). Fabrication of quaternized quinuclidine-based macroporous polymer gel with inherent antimicrobial activity.....	145
3(B).1. Introduction.....	146
3(B).2. Experimental.....	147
3(B).2.1. Materials	147
3(B).2.2. Synthesis of Quinuclidin-3-yl methacrylate	148

3(B).2.3. Synthesis of quaternary ammonium (QA) monomers	148
3(B).2.4. Fabrication of polymer gels	149
3(B).2.5. Swelling studies	149
3(B).2.6. Antimicrobial assay	150
3(B).2.7. SEM of bacteria.....	150
3(B).2.8. MD simulation	151
3(B).2.9. Characterization.....	151
3(B).2.10. Statistical analysis	152
3(B).3. Results and Discussion	152
3(B).4. Conclusion.	167
3(B).5. References	167
Chapter 4(A). 4-Dimethylaminopyridine based porous polymer microparticles for catalyzing the Baylis-Hillman reaction.	169
4(A).1. Introduction.	170
4(A).2. Experimental	172
4(A).2.1. Materials	172
4(A).2.2. Synthesis of DMAP-OH.....	172
4(A).2.3. Synthesis of 2-(methyl(pyridin-4-yl) amino) ethyl methacrylate	173
4(A).2.4. Synthesis of porous poly (DMAP-co-DVB) microparticles	173
4(A).2.5. Procedure for evaluating the catalytic effect of microparticles towards Baylis-Hillman reaction.	174
4(A).2.6. Procedure for the synthesis of a variety of Baylis-Hillman products.....	174
4(A).2.7. Computational Method	176
4(A).2.8. Characterization	177
4(A).3. Results and Discussion	177
4(A).4. Conclusion.....	195

4(A).5. References.....	195
Chapter 4(B). Fabrication of quaternized 4-dimethylaminopyridine based solvent-responsive macroporous polymer gel with inherent antimicrobial activity	198
4(B).1. Introduction	199
4(B).2. Experimental.....	200
4(B).2.1. Materials.....	200
4(B).2.2. Synthesis of DMAP-OH	201
4(B).2.3. Synthesis of 2-(methyl(pyridine-4-yl) amino) ethyl methacrylate	201
4(B).2.4. Synthesis of quaternary ammonium (QA) monomers	202
4(B).2.5. Fabrication of polymer gels	202
4(B).2.6. Swelling studies.....	203
4(B).2.7. Antimicrobial essay	203
4(B).2.8. SEM of bacteria	204
4(B).2.9. MD simulation	204
4(B).2.10. Characterization	205
4(B).2.11. Statistical analysis.....	205
4(B).3. Results and Discussion.....	206
4(B).4. Conclusion	223
4(B).5. References.....	223
Chapter 5. Conclusion and Future Perspective	226
BIODATA.....	230

LIST OF FIGURES

Figure 1.1 Porous polymer materials with tunable morphology, pore size and functionality.	3
Figure 1.2. Different approaches for the fabrication of porous polymer materials.	4
Figure 1.3. Applications of porous polymeric materials in different domains.	4
Figure 1.4. Different amine catalysts with varying basicity and nucleophilicity.	12
Figure 1.5. Mechanism of amine catalyzed Baylis-Hillman reaction.	14
Figure 1.6. Mechanism of amine catalyzed Knoevenagel condensation.	15
Figure 1.7. Macroporous polymer gel synthesis using porogen as a template.	18
Figure 1.8. Macroporous polymer gel synthesis using ice as a template (cryogelation).	18
Figure 1.9. Macroporous polymer gel synthesis using Pickering emulsion as a template.....	20
Figure 1.10. Macroporous polymer gel synthesis using gas foaming.	21
Figure 1.11. Macroporous polymer gel fabrication using 3D printing.....	22
Figure 1.12. Macroporous polymer gel fabrication using electrospinning.....	23
Figure 1.13. Interaction of quaternary ammonium compound with bacteria cell membrane.	27
 Figure 2(A).1. (a) Scheme showing synthesis of microparticles (b) FTIR spectra of DMA-P30, DMA-P50, DMA-P70 microparticles (c) FTIR spectra of DMA-NP30, DMA- NP50, and DMA-NP70 (d) ¹³ C solid state NMR spectrum for DMA-P70 (e) ¹⁵ N solid state NMR spectrum for DMA-P70.	47
Figure 2(A). 2. XPS analysis: (a) XPS wide spectra of DMA-P30, DMA-P50, DMA- P70 microparticles (b, b', b'') High resolution XPS of C(1s), N(1s), O(1s) for DMA-P30 (c, c', c'') High resolution XPS of C(1s), N(1s), O(1s) for DMA-P50 (d, d', d'') High resolution XPS of C(1s), N(1s), O(1s) for DMA-P70.....	48
Figure 2(A).3. BET isotherm for (a) DMA-P30, DMA-P50, DMA-P70 microparticles (b) DMA-NP30, DMA-NP50, and DMA-NP70.	49
Figure 2(A).4. Scanning electron micrographs of (a) DMA-P30 (a') DMA-NP30 (b) DMA-P50 (b') DMA-NP50 (c) DMA-P70 (c') DMA-NP70.	51

Figure 2(A).5. Particle size distribution bar graph (a) DMA-30 (b) DMA-NP30 (c) DMA-P50 (d) DMA-NP50 (e) DMA-P30 (f) DMA-NP30.....	52
Figure 2(A).6. (a) ^1H NMR and (b) ^{13}C NMR spectra of 2-(4-nitrobenzylidene) malononitrile.....	56
Figure 2(A).7. (a) ^1H NMR and (b) ^{13}C NMR spectra of 2-(4-chlorobenzylidene) malononitrile.....	57
Figure 2(A).8. (a) ^1H NMR and (b) ^{13}C NMR spectra of 2-(2,3-dichlorobenzylidene) malononitrile.....	58
Figure 2(A).9. (a) ^1H NMR and (b) ^{13}C NMR spectra of 2-(2,5-dibromobenzylidene) malononitrile.....	59
Figure 2(A).10. (a) ^1H NMR and (b) ^{13}C NMR spectra of 2-(4-cyanobenzylidene) malononitrile.....	60
Figure 2(A).11. (a) ^1H NMR and (b) ^{13}C NMR spectra of 2-benzylidenemalononitrile.	61
Figure 2(A).12. (a) ^1H NMR and (b) ^{13}C NMR spectra of 2-(4-hydroxybenzylidene) malononitrile.....	62
Figure 2(A).13. (a) ^1H NMR and (b) ^{13}C NMR spectra of 2-(4-methoxybenzylidene) malononitrile.....	63
Figure 2(A).14. Representation of clusters of poly(DMA-DVB) microparticles (a) DMA1-DVB3 cluster, (b) DMA2-DVB2 cluster, and (c) DMA3-DVB1 cluster.	64
Figure 2(A).15. (a) The mechanism of the Knoevenagel reaction of malononitrile and p-nitrobenzaldehyde using microparticles based on DMAEMA and DVB (b) DFT calculated ΔG (eV) for each reaction step during the Knoevenagel condensation with DMA3-DVB1 cluster as catalyst in water at 298.15 K.	65
Figure 2(A).16. DFT optimised structures of all intermediates and DMA3-DVB1 cluster before and after protonation from malononitrile.	66
Figure 2(A).17. Gibbs free energy change at 298.15 K and 324.14 K. for each reaction step of the Knoevenagel reaction of p-nitrobenzaldehyde & malononitrile by using of DMA-DVB as a catalyst.	67
Figure 2(A).18. Recyclability of catalytic performance of DMA-P70 microparticles for Knoevenagel reaction between 4-nitrobenzaldehyde and malononitrile.	69

Figure 2(B).1. Reaction scheme representing the synthesis of quaternary ammonium monomers differing in chain length of alkyl substituent.	81
Figure 2(B).2. (a) ^1H NMR and (b) ^{13}C NMR were recorded for QA monomer bearing butyl chain in D_2O solvent.	82
Figure 2(B).3. (a) ^1H NMR and (b) ^{13}C NMR were recorded for QA monomer bearing hexyl chain in D_2O solvent.	83
Figure 2(B).4. (a) ^1H NMR and (b) ^{13}C NMR were recorded for QA monomer bearing octyl chain in D_2O solvent.	84
Figure 2(B).5. Reaction scheme representing the fabrication of macroporous antimicrobial polymeric gel (MAPG) bearing alkyl group of different chain lengths via free radical polymerization at sub-zero temperature.	85
Figure 2(B).6. Swollen MAPG based on NMe ₂ (a) 2.5 eq. (b) 5 eq. (c) 10 eq. (g) 15 eq.	85
Figure 2(B).7. Swollen MAPG based on C ₄ (a) 2.5 eq. (b) 5 eq. (c) 10 eq. (g) 15 eq.	86
Figure 2(B).8. Swollen MAPG based on C ₆ (a) 2.5 eq. (b) 5 eq. (c) 10 eq. (g) 15 eq.	86
Figure 2(B).9. Swollen MAPG based on C ₈ (a) 2.5 eq. (b) 5 eq. (c) 10 eq. (g) 15 eq.	86
Figure 2(B).10. FTIR spectra of MAPGs (a) NMe ₂ -2.5, C ₄ -2.5, C ₆ -2.5, C ₈ -2.5 (b) NMe ₂ -5, C ₄ -5, C ₆ -5, C ₈ -5 (c) NMe ₂ -10, C ₄ -10, C ₆ -10, C ₈ -10 (d) NMe ₂ -15, C ₄ -15, C ₆ -15, C ₈ -15.	87
Figure 2(B).11. (a) XPS full spectra of NMe ₂ -2.5, C ₄ -2.5, C ₆ -2.5, and C ₈ -2.5 gel samples; High resolution XPS spectra of NMe ₂ -2.5, C ₄ -2.5, C ₆ -2.5, and C ₈ -2.5 gel samples (b) N(1s) (c) C(1s) (d) O(1s).	88
Figure 2(B).12. SEM micrographs and nitrogen mapping from EDX of MAPG (a,a') C ₄ having 2.5 eq. crosslinker (b,b') C ₄ having 5 eq. crosslinker (c,c') C ₄ having 10 eq. crosslinker (d,d') C ₄ having 15 eq. crosslinker (e,e') C ₆ having 2.5 eq. crosslinker (f,f') C ₆ having 5 eq. crosslinker (g,g') C ₆ having 10 eq. crosslinker (h,h') C ₆ having 15 eq. crosslinker (i,i') C ₈ having 2.5 eq. crosslinker (j,j') C ₈ having 5 eq. crosslinker (k,k') C ₈ having 10 eq. crosslinker (l,l') C ₈ having 15 eq. crosslinker.	90

Figure 2(B).13. SEM micrographs and nitrogen mapping from EDX of MAPG (a, a') NMe2 having 2.5 eq. crosslinker (b, b') NMe2 having 5 eq. crosslinker (c, c') NMe2 having 10 eq. crosslinker (d, d') NMe2 having 15 eq. crosslinker.	91
Figure 2(B).14. Swelling degree for MAPG bearing alkyl group of different chain lengths and at varying crosslinking ratios.	93
Figure 2(B).15. Swelling degree versus time for MAPG (a) NMe2 (2.5 eq., 5 eq., 10 eq., 15 eq.) (b) C4 (2.5 eq., 5eq., 10eq., 15 eq.) (c) C6 (2.5 eq., 5eq., 10eq., 15 eq.) (d) C8 (2.5 eq., 5eq., 10 eq., 15 eq.).	93
Figure 2(B).16. Young's modulus (E) for MAPG bearing alkyl group of different chain length and at varying cross-linking ratio subjected to compression test.	95
Figure 2(B).17. Strain-stress plots of the NMe2-based MAPGs in a compression test. (a) NMe2-2.5 eq. (b) NMe2-5 eq. (c) NMe2-10 eq. (d) NMe2-15 eq.	96
Figure 2(B).18. Strain-stress plots of the C4-based MAPGs in compression test. (a) C4-2.5 eq. (b) C4-5 eq. (c) C4-10 eq. (d) C4-15 eq.	97
Figure 2(B).19. Strain-stress plots of the C6-based MAPGs in compression test, (a) C6-2.5 eq. (b) C6-5 eq. (c) C6-10 eq. (d) C6-15 eq.	98
Figure 2(B).20. Strain-stress plots of the C8-based MAPGs in compression test. (a) C8-2.5 eq. (b) C8-5 eq. (c) C8-10 eq. (d) C8-15 eq.	99
Figure 2(B).21. Digital photograph of C8-2.5 and C8-5 gels under compression, I- Initial state, II- under compression, III- after removal of load.	100
Figure 2(B).22. (a) Ultimate tensile strength of C8 gels (b) %elongation for C8 gels (c) Digital photograph of the tensile sample for C8-2.5, C8-5, C8-10, C8-15 gels.	100
Figure 2(B).23. Tensile stress vs strain curve of the C8-based MAPGs during the tensile testing (a) C8-2.5 eq. (b) C8-5 eq. (c) C8-10 eq. (d) C8-15 eq.	101
Figure 2(B).24. Antimicrobial performance of gels against (a) <i>B. subtilis</i> (b) <i>S. aureus</i> (c) <i>E. coli</i> (d) <i>P. aeruginosa</i>	104
Figure 2(B).25. (a) Flow cytometry was performed using PI stain with <i>E. coli</i> treated with different polymeric gels. (b) Confocal microscopy was performed using PI stain with <i>E. coli</i> treated with different polymeric gels.	107
Figure 2(B).26. (a) Flow cytometry was performed using PI stain with <i>S. aureus</i> treated with different polymeric gels. (b) Confocal microscopy was performed using PI stain with <i>S. aureus</i> treated with different polymeric gels.	108

Figure 3(A).1. (a) Reaction scheme representing the synthesis of quinuclidine-3-yl methacrylate monomers (b) Reaction scheme representing the fabrication of microparticles by distillation precipitation polymerization.....	121
Figure 3(A).2. (a) ^1H NMR spectrum of quinuclidine-3-yl methacrylate (QM) (b) ^{13}C NMR spectrum of quinuclidine-3-yl methacrylate (QM).....	122
Figure 3(A).3. (a) FTIR spectrum of nonporous microparticles. (b) FTIR spectrum of porous microparticles.....	123
Figure 3(A).4. (a) ^{13}C solid-state NMR spectrum of Porous microparticles comprising approximately 70% of catalytic moiety (designated as P70) (b) ^{13}C solid-state NMR spectrum of porous microparticles without catalytic moiety (designated as P0).....	124
Figure 3(A).5. BET isotherm of (a) non-porous and (b) porous polymer microparticles.	125
Figure 3(A).6. Scanning electron microscopic graphs of microparticles designated as (a) P ₀ (b) P ₃₀ , (c) P ₅₀ , (d) P ₇₀	127
Figure 3(A). 7. Scanning electron microscopic graphs of microparticles designated as (a) NP ₀ , (b) NP ₃₀ , (c) NP ₅₀ , (d) NP ₇₀	128
Figure 3(A).8. Particle size distribution bar graph (a) NP ₀ (b) P ₀ (c) NP ₃₀ (d) P ₃₀ (e) NP ₅₀ (f) P ₅₀ (g) NP ₇₀ (h) P ₇₀	129
Figure 3(A).9. (a) Reaction scheme showing Baylis- hillman reaction between p-nitro benzaldehyde and acrylonitrile (b) Proposed mechanism for accelerated Baylis-Hillman reaction.....	130
Figure 3(A).10. (a) ^1H NMR spectrum for 2-(hydroxy(4-nitrophenyl) methyl) acrylonitrile (b) ^{13}C NMR spectrum for 2-(hydroxy(4-nitrophenyl) methyl) acrylonitrile in CDCl ₃ solvent.	134
Figure 3(A).11. (a) ^1H NMR spectrum for 2-(hydroxy(2-nitrophenyl) methyl) acrylonitrile (b) ^{13}C NMR spectrum for 2-(hydroxy(2-nitrophenyl) methyl) acrylonitrile in CDCl ₃ solvent.	135
Figure 3(A).12. (a) ^1H NMR spectrum for 2-(hydroxy(3-nitrophenyl) methyl) acrylonitrile (b) ^{13}C NMR spectrum for 2-(hydroxy(3-nitrophenyl) methyl) acrylonitrile in CDCl ₃ solvent.	136
Figure 3(A).13. (a) ^1H NMR spectrum for 2-(hydroxy(4-cyanophenyl) methyl) acrylonitrile (b) ^{13}C NMR spectrum for 2-(hydroxy(4-cyanophenyl) methyl) acrylonitrile in CDCl ₃ solvent.	137

Figure 3(A).14. (a) ^1H NMR spectrum for 2-(hydroxy(2,3-dichlorophenyl) methyl) acrylonitrile (b) ^{13}C NMR spectrum for 2-(hydroxy(2,3-dichlorophenyl) methyl) acrylonitrile in CDCl_3 solvent.	138
Figure 3(A).15. (a) ^1H NMR spectrum for 2-(hydroxy(4-chlorophenyl) methyl) acrylonitrile (b) ^{13}C NMR spectrum for 2-(hydroxy(4-chlorophenyl) methyl) acrylonitrile in CDCl_3 solvent.	139
Figure 3(A).16. (a) ^1H NMR spectrum for 2-(hydroxy(4-bromophenyl) methyl) acrylonitrile (b) ^{13}C NMR spectrum for 2-(hydroxy(4-bromophenyl) methyl) acrylonitrile in CDCl_3 solvent.	140
Figure 3(A).17. Recyclability of catalytic performance of microparticles containing 70 % QM, designated as P ₇₀ for Baylis-Hillman reaction between 4-nitrobenzaldehyde and acrylonitrile.	141
 Figure 3(B).1. (a) Synthesis of quinuclidin-3-yl methacrylate (b) Synthesis of quaternary ammonium monomers (designated as QMC4, QMC6, QMC8, and QMC12) (c) Synthesis of polymer gels designated as QGC4, QGC6, QGC8, and QGC12. ..	153
Figure 3(B).2. (a) ^1H NMR spectrum of quinuclidine-3-yl methacrylate (b) ^{13}C NMR spectrum of quinuclidine-3-yl methacrylate.	154
Figure 3(B).3. (a) ^1H NMR spectrum of quaternized quinuclidine monomer designated as QMC4 (b) ^{13}C NMR spectrum of QMC4 monomer.	155
Figure 3(B).4. (a) ^1H NMR spectrum of quaternized quinuclidine monomer designated QMC6 (b) ^{13}C NMR spectrum of QMC6 monomer.	156
Figure 3(B).5. (a) ^1H NMR spectrum of quaternized quinuclidine monomer designated QMC8 (b) ^{13}C NMR spectrum of QMC8 monomer.	157
Figure 3(B).6. (a) ^1H NMR spectrum of quaternized quinuclidine monomer designated QMC12 (b) ^{13}C NMR spectrum of QMC12 monomer.	158
Figure 3(B).7. ^{13}C CP MAS solid state NMR spectrum of (a) QGC4 (b) QGC6 (c) QGC8 (d) QGC12.....	159
Figure 3(B).8. (a) FTIR spectra, and (b) XPS spectra of the gels designated as QGC4, QGC6, QGC8, QGC12.	160
Figure 3(B).9. FESEM images of the polymer gels (a) QGC4 (b) QGC6 (c) QGC8 (d) QGC12.	161

Figure 3(B).10. Swelling ratio of the gels designated as QGC4, QGC6, QGC8, QGC12 in water.	162
Figure 3(B).11. Antimicrobial performance of the gels against (a) <i>S. aureus</i> and (b) <i>E. coli</i>	163
Figure 3(B).12. SEM micrographs for the <i>E. coli</i> (a) Control (b) Treated with QGC4 gel (c) Treated with QGC6 gel (d) Treated with QGC8 gel (e) Treated with QGC12 gel.	164
Figure 3(B).13. SEM micrographs for the <i>S. aureus</i> (a) Control (b) Treated with QGC4 gel (c) Treated with QGC6 gel (d) Treated with QGC8 gel (e) Treated with QGC12 gel.	165
Figure 3(B).14. Molecular models of the quaternized quinuclidine derivatives and the DOPE/DOPG (4: 1) <i>E. Coli</i> bacterial membrane.	165
Figure 3(B).15. Interaction energies between quaternized quinuclidine derivatives and the charged lipid components (DOPE and DOPG).	166
Figure 4(A).1. Synthesis of (a) DMAP-OH (b) 2-(methyl(pyridine-4-yl) amino) ethyl methacrylate (c) Polymer microparticles.	178
Figure 4(A).2. (a) ¹ H NMR spectrum of DMAP-based alcohol designated DMAP-OH (b) ¹³ C-NMR spectrum of DMAP-OH.	179
Figure 4(A).3. (a) ¹ H NMR spectrum of 2-(methyl(pyridine-4-yl) amino) ethyl methacrylate.	180
Figure 4(A).4. (a) FTIR spectra of microparticles designated as DMAP ₃₀ , DMAP ₅₀ , DMAP ₇₀ (b) ¹³ C CP MAS solid state NMR spectra of DMAP ₃₀ (c) ¹³ C CP MAS solid state NMR spectra of DMAP ₅₀ (c) ¹³ C CP MAS solid state NMR spectra of DMAP ₇₀	181
Figure 4(A).5. (a) XPS Spectra, and (b) BET isotherm of microparticles designated as DMAP ₃₀ , DMAP ₅₀ , and DMAP ₇₀	182
Figure 4(A).6. SEM micrographs of microparticles designated as (a) DMAP ₃₀ (b) DMAP ₅₀ (c) DMAP ₇₀	184
Figure 4(A).7. (a) Reaction scheme showing Baylis- hillman reaction between p-nitro benzaldehyde and acrylonitrile (b) Proposed mechanism for accelerated Baylis-Hillman reaction.	185

Figure 4(A).8. (a) ^1H NMR spectrum for 2-(hydroxy(4-nitrophenyl) methyl) acrylonitrile and (b) ^{13}C NMR spectrum for 2-(hydroxy(4-nitrophenyl) methyl) acrylonitrile in CDCl_3 solvent.	188
Figure 4(A).9. (a) ^1H NMR spectrum 2-(hydroxy(4-chlorophenyl) methyl) acrylonitrile for and (b) ^{13}C NMR spectrum for 2-(hydroxy(4-chlorophenyl) methyl) acrylonitrile in CDCl_3 solvent.....	189
Figure 4(A).10. (a) ^1H NMR spectrum for 2-(hydroxy(4-cyanophenyl) methyl) acrylonitrile and (b) ^{13}C NMR spectrum for 2-(hydroxy(4-cyanophenyl) methyl) acrylonitrile in CDCl_3 solvent.	190
Figure 4(A).11. (a) ^1H NMR spectrum for 2-(hydroxy(4-bromophenyl) methyl) acrylonitrile and (b) ^{13}C NMR spectrum for 2-(hydroxy(4-bromophenyl) methyl) acrylonitrile in CDCl_3 solvent.	191
Figure 4(A).12. (a) ^1H NMR spectrum for 2-(hydroxy(2,3-dichlorophenyl) methyl) acrylonitrile and (b) ^{13}C NMR spectrum for 2-(hydroxy(2,3-dichlorophenyl) methyl) acrylonitrile in CDCl_3 solvent.	192
Figure 4(A).13. Recyclability of catalytic performance of microparticles designated as DMAP ₇₀ for Baylis-Hillman reaction between 4-nitrobenzaldehyde and acrylonitrile.	193
Figure 4(A).14. Representation of cluster of poly(DMAP-DVB) microparticles (one unit of 2-(methyl(pyridin-4-yl) amino) ethyl methacrylate attached to one unit of divinylbenzene).....	193
Figure 4(A).15. DFT calculated ΔG (eV) for each reaction step during the Baylis-Hillman reaction of p-nitro benzaldehyde and acrylonitrile with DMAP-DVB cluster as a catalyst in water.....	194
 Figure 4(B).1. (a) Synthesis of DMAP-OH (b) Synthesis of 2-(methyl(pyridine-4-yl) amino) ethyl methacrylate (c) Synthesis of quaternary ammonium monomers (designated as DMAP-C4, DMAP-C6, DMAP-C8, and DMAP-C12) (d) Synthesis of polymer gels designated as DGC4, DGC6, DGC8, and DGC12.....	206
Figure 4(B).2. (a) ^1H NMR spectrum of DMAP-based alcohol designated as DMAP-OH (b) ^{13}C -NMR spectrum of DMAP-OH.....	207
Figure 4(B).3. ^1H NMR spectrum of 2-(methyl(pyridine-4-yl) amino) ethyl methacrylate.	208

Figure 4(B).4. (a) ^1H NMR spectrum of quaternized DMAP monomer designated as DMAP-C4 (b) ^{13}C -NMR spectrum of DMAP-C4.	209
Figure 4(B).5. ^1H NMR spectrum of quaternized DMAP monomer designated as DMAP-C6 (b) ^{13}C NMR spectrum of DMAP-C6.	210
Figure 4(B).6. (a) ^1H NMR spectrum of quaternized DMAP monomer designated as DMAP-C8 (b) ^{13}C NMR spectrum of DMAP-C8.	211
Figure 4(B).7. (a) ^1H NMR spectrum of quaternized DMAP monomer designated as DMAP-C12 (b) ^{13}C NMR spectrum of DMAP-C12.	212
Figure 4(B).8. ^{13}C CP MAS solid state NMR spectrum of (a) DGC4 (b) DGC6 (c) DGC8 (d) DGC12.	213
Figure 4(B).9. (a) FTIR spectra, and (b) XPS spectra of the gels designated as DGC4, DGC6, DGC8, and DGC12.	214
Figure 4(B).10. FESEM images of the gels (a) DGC4 swollen in ethanol (a') DGC4 swollen in water (b) DGC6 swollen in ethanol (b') DGC6 swollen in water (c) DGC8 swollen in ethanol (c') DGC8 swollen in water, (d) DGC12 swollen in ethanol (d') DGC12 swollen in water.	215
Figure 4(B).11. (a) Swelling ratio of the gels designated as DGC4, DGC6, DGC8, DGC12 in water and ethanol (b) digital photograph of the fully swollen gels in ethanol and water.	216
Figure 4(B).12. (a) Solvent responsive study of gels DGC8 and DGC12 in water and ethanol (b) Transmittance of the gels DGC8 and DGC12 in water and ethanol.	217
Figure 4(B).13. Antimicrobial performance of the gels against (a) <i>S. aureus</i> and (b) <i>E. coli</i>	219
Figure 4(B).14. SEM micrographs for the <i>E. coli</i> (a) Control (b) Treated with DGC4 gel (c) Treated with DGC6 gel (d) Treated with DGC8 gel (e) Treated with DGC12 gel.	220
Figure 4(B).15. SEM micrographs for the <i>S. aureus</i> (a) Control (b) Treated with DGC4 gel (c) Treated with DGC6 gel (d) Treated with DGC8 gel (e) Treated with DGC12 gel.	221
Figure 4(B).16. Molecular models of the quaternized DMAP and the DOPE/DOPG (4:1) <i>E. Coli</i> bacterial membrane.	222
Figure 4(B).17. Interaction energies between quaternized DMAP and the charged lipid components (DOPE and DOPG).	222

LIST OF TABLES

Table 1.1. Chemical structures, synthesis method, porogen, and accessible surface area of porous polymer microparticles.	8
Table 1.2. Chemical composition of porous polymer microparticles, catalytic moiety, reaction, and conversion.	10
Table 2(A).1. Composition of DMAEMA, divinyl benzene and the % yield porous microparticles prepared with 2 wt. % AIBN in 80 mL acetonitrile and their sample designation.....	41
Table 2(A).2. Composition of quinuclidine monomer, divinyl benzene and the % yield nonporous microparticles prepared with 2 wt. % AIBN in 80 mL acetonitrile and their sample designation.	41
Table 2(A).3. Number average particle size, weight average particle size, polydispersity index, BET accessible surface area, BJH pore size (determined from the desorption curve), and total pore volume for microparticles.....	50
Table 2(A).4. Catalytic performance of microparticles designated as DMA-P70 on varying water fraction in reaction medium (DMSO/H ₂ O) to perform Knoevenagel reaction of 4-nitrobenzaldehyde and malononitrile at 25 °C for 24 h.	53
Table 2(A).5. Catalytic performance of porous microparticles (DMA-P70, DMA-P50, DMA-P30) using a variety of solvents for Knoevenagel reaction of 4-nitrobenzaldehyde and malononitrile at 25 °C and 50 °C.	54
Table 2(A).6. Catalytic performance of nonporous microparticles (DMA-NP70, DMA-NP50, DMA-NP30) using a variety of solvents to perform the Knoevenagel Condensation of 4-Nitrobenzaldehyde and malononitrile at 25 °C as well as at 50 °C.	54
Table 2(A).7. Catalytic performance of microparticles using ethanol as solvent for Knoevenagel reaction of 4-nitrobenzaldehyde and malononitrile at 50 °C. ^a % conversion determined from ¹ H NMR spectra, ^b isolated yield.	55
Table 2(A).8. ΔG values derived for four elementary reaction steps at 298.15 K and 324.15 K using three DMA-DVB clusters designated as DMA3-DVB1, DMA2-DVB2,	

and DMA1-DVB3 catalyst in four different solvents (water, DMSO, methanol, ethanol).	67
Table 2(A).9. ΔH values derived for four elementary reaction steps at 298.15 K and 324.15 K using three DMA-DVB clusters designated as DMA3-DVB1, DMA2-DVB2, and DMA1-DVB3 catalyst in four different solvents (water, DMSO, methanol, ethanol).	68
Table 2(B).1. Composition of various MAPG containing different QA monomers as well as crosslinker amount.	77
Table 2(B).2. Modulus (E), swelling degree, and antimicrobial activity of MAPGs against <i>E. coli</i> , <i>P. aeruginosa</i> , <i>S. aureus</i> , <i>B. subtilis</i>	104
Table 3(A).1. Composition of quinuclidine monomer, divinyl benzene and the % yield nonporous and porous microparticles prepared with 2 wt. % AIBN in 80 mL acetonitrile and their sample designation.	116
Table 3(A).2. Number average particle size, weight average particle size, polydispersity index, BET accessible surface area, BJH pore size (determined from desorption curve), and total pore volume for porous as well as nonporous microparticles.....	126
Table 3(A).3. Catalytic performance of microparticles designated as P70 and NP70 on varying water fraction and type of organic solvent in reaction medium to perform Baylis-Hillman reaction of 4-nitrobenzaldehyde and acrylonitrile at 50 °C for 12 h. ...	131
Table 3(A).4. Catalytic performance of microparticles using DMSO: H ₂ O (7:3) with differing in catalytic moiety loading in reaction medium to perform Baylis-Hillman reaction of 4-nitrobenzaldehyde and acrylonitrile at 50 °C as well as at room temperature for 12 h.....	132
Table 3(A).5. Synthesis of Baylis-Hillman products using P ₇₀ Catalyst. ^a % Conversion (determined from ¹ H-NMR), ^b % yield.	133
Table 3(B).1. Composition of various gels containing different quaternary ammonium monomers.	149

Table 4(A).1. Composition of DMAP monomer, divinyl benzene, and the % yield porous microparticles prepared with 2 wt. % AIBN in 80 mL acetonitrile and their sample designation.	174
Table 4(A).2. Number average particles size, weight average particles size, polydispersity index, BET accessible surface area, BJH pore size (determined from desorption curve), and total pore volume for porous microparticles.	183
Table 4(A).3. Catalytic performance of microparticles using DMSO: H ₂ O (7:3) with differing in catalytic moiety loading in reaction medium to perform Baylis-Hillman reaction of 4-nitrobenzaldehyde and acrylonitrile at 50 °C as well as at room temperature for 16 h.....	186
Table 4(A).4. Synthesis of Baylis-Hillman products using P70 Catalyst. ^a % Conversion (determined from ¹ H NMR), ^b % yield.	187
 Table 4(B).1. Composition of various gels containing different quaternary ammonium monomers.	 203

LIST OF ABBREVIATION

AIBN	Azobisisobutyronitrile
OEG-DMA	Oligoethylene dimethacrylate
DVB	Divinyl benzene
PDI	Polydispersity index
<i>E. Coli</i>	Escherichia coli
<i>S. aureus</i>	Staphylococcus aureus
<i>B. subtilis</i>	Bacillus subtilis
<i>P. aeruginosa</i>	Pseudomonas aeruginosa
NMR	Nuclear Magnetic Resonance
ACN	Acetonitrile
UTM	Universal Testing Machine
CLSM	Confocal laser scanning microscopy
FTIR	Fourier-transform infrared
DFT	Density functional theory
DMAEMA	2-(Dimethylamino)ethyl methacrylate
SEM	Scanning electron microscopy
THF	Tetrahydrofuran
XPS	X-ray photoelectron microscopy
DOPE	1,2-Dioleoyl-sn-Glycero-3- Phosphoethanolamine
DOPG	1,2-Dioleoyl-sn-Glycero-3-[Phospho- rac-(1-glycerol)]
DMSO	Dimethyl sulfoxide
<i>E</i>	Young's modulus
θ	Swelling degree