TECHNICAL REPORT
NATICK/TR-24/006

AD _____

COVALENT GRAFTING OF DURABLE AND OPTICALLY CLEAR ANTIFOGGING COPOLYMER FILMS TO PROTECTIVE COMBAT GLASSES

by
Professor Jason Locklin
Qiaohong Liu
Madison Smith
Caitlin Cato
Grant Crane
and
Ryan Maynard

University of Georgia (UGA) Research Foundation
Athens, GA 30602-1589

March 2024

Final Report
February 2019 – November 2021

Prepared for
U.S. Army Combat Capabilities Development Command Soldier Center
Natick, Massachusetts 01760-5019

DISCLAIMERS

The findings contained in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of trade names in this report does not constitute an official endorsement or approval of the use of such items.

DESTRUCTION NOTICE

For Classified Documents:

Follow the procedures in DoD 5200.22-M, Industrial Security Manual, Section II-19 or DoD 5200.1-R, Information Security Program Regulation, Chapter IX.

For Unclassified/Limited Distribution Documents:

Destroy by any method that prevents disclosure of contents or reconstruction of the document.

REPORT DOCUMENTATION PAGE

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED	
13-03-2024	Final	START DATE February 2019	END DATE November 2021

4. TITLE AND SUBTITLE

COVALENT GRAFTING OF DURABLE AND OPTICALLY CLEAR ANTIFOGGING COPOLYMER FILMS TO PROTECTIVE COMBAT GLASSES

5a. CONTRACT NUMBER	5b. GRANT NUMBER	5c. PROGRAM ELEMENT NUMBER
W911QY-19-P-0013		
5d. PROJECT NUMBER	**5e. TASK NUMBER**	**5f. WORK UNIT NUMBER**

6. AUTHOR(S)

Professor Jason Locklin, Qiaohong Liu, Madison Smith, Caitlin Cato, Grant Crane, Ryan Maynard

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of Georgia (UGA) Research Foundation
310 East Campus Road
Athens, GA 30602-1589

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

US Army Combat Capabilities Development Command Soldier Center
ATTN: FCDD-SCD-PMI
10 General Greene Avenue
Natick, MA 01760-5019

10. SPONSOR/MONITOR'S ACRONYM(S)

DEVCOM SC

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

NATICK/TR-24/006

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Fogging of goggles, glasses, and other optical devices can lead to numerous practical issues. Because of this, significant work has been done to develop antifogging coatings for various substrates. However, many of the current methods involve expensive and challenging application techniques with precise curing methods. In this report, the University of Georgia (UGA) New Materials Institute describes the attempted development of a zwitterionic antifogging copolymer that can be covalently grafted to any substrate with an abstractable hydrogen. Copolymers were made that originally had excellent antifogging characteristics and durability, but there were challenges in reproducing the copolymer composition and coating formulation that led to continued antifogging and durable coatings. The coatings were inconsistent in several ways, and ultimately resulted in subpar performance of the antifogging films.

15. SUBJECT TERMS

ANTIFOG	ABRASION RESISTANCE	CHEMICAL	COATINGS
COPOLYMER	COVALENT GRAFTING	CROSSLINKING	EYEWEAR
FOG	GLASSES	GOGGLES	HYDROPHILIC
HYDROPHOBIC	LENSES	MONOMER	PHOTO CHEMICAL
POLYMER	POLYCARBONATE	TERPOLYMER	UV IRRADIATION
ZWITTERIONIC			

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES
a. REPORT	b. ABSTRACT	C. THIS PAGE		
U	U	U	UU	28

19a. NAME OF RESPONSIBLE PERSON	19b. PHONE NUMBER *(Include area code)*
Michelle Markey	(508) 206-3196

This page intentionally left blank

Table of Contents

List of Figures

List of Tables

Executive Summary

This document describes the introduction and development of an antifogging thin film for application to soldier eyewear systems. The work was performed from February 2019 through November 2021 by the University of Georgia – New Materials Institute under contract W911QY19P0013 with the University of Georgia Research Foundation for the U.S. Army Combat Capabilities Development Command Soldier Center (DEVCOM SC). Covalent grafting of zwitterionic copolymers using ultraviolet (UV)-curing was investigated on many different plastic and glass substrates. In early experiments, there was consistent and repeatable success in synthesizing and curing a high-performance antifogging copolymer. However, after the initial successes, the technology's performance was suddenly unable to be replicated. Much of the document covers the troubleshooting of the technology and the methods that were utilized to attempt to develop a deployable technology. Though the reasons for the sudden lack of performance are still unknown, a variety of troubleshooting routes have been employed to elucidate the cause.

FINAL TECHNICAL REPORT: COVALENT GRAFTING OF DURABLE AND OPTICALLY CLEAR ANTIFOGGING COPOLYMER FILMS TO PROTECTIVE COMBAT GLASSES

Introduction

The work for this project was performed by the University of Georgia (UGA) – New Materials Institute from February 2019 to November 2021 for the Combat Capabilities Development Command Soldier Center (DEVCOM SC) with the purpose of developing an antifogging thin film for application to soldier eyewear systems.

Formation of fog due to water vapor condensation on a surface due to a temporary change in temperature and humidity leads to many problems in practical applications, including windshields, eyeglasses, safety glasses, and optical instruments.[1-5] To alleviate fog formation, there are three general strategies used to prepare antifogging films, each with its own advantages and disadvantages. One conventional approach uses photo-active inorganic nanoparticles such as titanium dioxide (TiO_2) and zinc oxide (ZnO) that become super-hydrophilic under ultraviolet (UV) light exposure.[6-9] Others include different fabrication methods such as layer-by-layer assembly or electrostatic spinning, which aim to modify the chemical environment and geometric microstructure of the surface into a nonporous or textured film, which will absorb water and facilitate the spread of water on the surface.[10-13] Both of these approaches described above require multiple steps, harsh reactants, and/or post treatments, all of which can limit practical application in everyday use.[14-15] A third approach, which involves simple deposition of hydrophilic polymer coatings on to various substrates, is a very promising candidate that provides a low cost and simple process with high efficiency.[16-17] Nevertheless, the preparation of highly transparent and robust superhydrophobic polymer coatings remained a challenge. For instance, there are reports of obtaining superhydrophobic coatings using spin coating,[2, 18] layer-by-layer assembly,[19] and polymer brushes.[15, 20.] However, all of these methods are difficult to scale and implement commercially.

Zwitterionic polymers have attracted attention due to their strong hydration capacity and have been widely used as biomimetic antifouling materials in marine and biomedical applications.[15, 21-22] The dipole arrangement of the water molecule in the hydration shell formed via electrostatic interactions with the charged groups of the zwitterion are close to that of free water. Therefore, adsorbed water can create a continuous or near-continuous film, minimizing scattering events and preserving the optical transmission of the substrate.[19, 23] However, due to the high solubility of the zwitterionic polymers, these coatings are easily delaminated or dissolved in the presence of water, which is a limitation of this approach.[14] To permanently attach zwitterionic polymer thin films to a substrate, there are several reports utilizing layer-by-layer methods or polymer brush techniques,[15, 19-20, 24] but these still have many challenges in translation from small laboratory substrates to scale mass production. Coatings that are grafted through either chemical or photochemical crosslinking are considered to be an effective and reasonable method for modifying polymer materials on substrates through covalent bonding.[25-26] The ability of

benzophenone (BP) to act as a cross-linking agent and abstract hydrogen from a suitable hydrogen donor has been well studied and utilized in various chemical systems for many years.[27-28] BP is an ideal choice for crosslinking organic thin films because it can be activated using mild UV light (345 – 365 nm), avoiding oxidative damage to either the polymer or substrate that can occur upon exposure to higher energy UV. The BP moiety is more chemically robust than other organic cross-linkers and reacts preferentially with C-H bonds in a wide range of different chemical environments. When irradiated with UV light, an electron from the n-orbital on the carbonyl of BP is exited to π*-orbital to a biradical triplet excited state that can abstract a hydrogen atom from a neighboring aliphatic carbon-hydrogen bond to form a new carbon-carbon bond. This triplet state also has unusually high reactivity for H atoms located alpha to electron donating heteroatoms (nitrogen and oxygen). This photoreaction has recently been used to attach thin polymer layers to metal and oxide surfaces,[29-31] along with applications ranging from organic semiconductors,[32] microfluidic devices,[33-34] hydrogels,[29, 35] and biosensors.[36-37] Because of these advantages, UGA previously developed antimicrobial copolymers containing hydrophobic N-alkyl and BP moiety on a polyethyleneimine backbone;[38] anti-icing copolymers consisting of hexafluorobutyl, benzophenone, and nanoparticles;[39] and antifouling copolymers containing zwitterionic monomers and BP.[40] All of these systems exhibit fast crosslinking kinetics and high abrasion resistance. In this study, a zwitterionic terpolymer (2-methacryloyloxyethyl phosphorylcholine-cobutyl methacrylate-co-benzophenone (BPMPC)) was synthesized and covalently grafted to alkyl-modified glass and plastic lenses with UV irradiation to increase the durability of the coating. Numerous experiments, such as crosslinking kinetics, Atomic Force Microscopy (AFM), and Attenuated Total Reflection Fourier-Transform Infrared Spectroscopy (ATR-FTIR) were performed to optimize the coating for use in applications to Soldier eyewear systems. However, no optimized process was achieved in the study that would allow for realistic application of this technology to current eyewear systems.

Methods, Assumptions, and Procedures

1. Procedure for Alkyl Modification of Glass and Quartz Slides:

   Glass Microscope Slides (Fischer Scientific) or Quartz Microscope Slides (AdValue Technology) were first cleaned by sonication for 5 min each in water, isopropyl alcohol, then acetone followed by plasma cleaning (Harrick Plasma PDC-32G, Argon Gas) and treatment with isobutyltrichlorosilane (i-BTS) in toluene (10 mmol) overnight.

2. Procedure for Spin Coating of Polymers:

   Polymers were dissolved at the appropriate concentration (often 20 mg/mL) and spin coated at 2,000 rpm for 30 s to produce a uniform and thin film.

3. Procedure for Spray Coating of Polymers:

   Polymers were dissolved in 200 proof ethanol at 2 mg/mL. The polymers were transferred to a reagent sprayer (Chemglass Scientific – 125 mL) and house air was used to spray the polymer solution to evenly coat the desired substrate. The substrates were allowed to dry before further UV curing or testing.

4. Procedure for Synthesis of Polymers:

   Appropriate amounts of monomer, initiator, and solvent were added to a flat-bottom Schlenk flask with a stir bar. The flask was appropriately degassed (via either sparging with Argon for 30-60 min, or five freeze-pump-thaw cycles) before heating at 65 °C for 18 h.

5. Procedure for UV Irradiation of Polymers:

   After the polymers were properly coated on various substrates, the samples were irradiated with a UV oven (Fisher Scientific FB-UVXL-1000) at a distance that provided a known intensity of light of approximately 2 Mw/cm^2. The intensity was measured with a UV Intensity Meter (OAI UV 306).

6. Procedure for Testing Antifog Ability of Thin Films:

   Films were coated onto a substrate, as previously mentioned. A hot water bath (approximately 80 °C) was prepared, and the substrates were held over the water bath at approximately 10 cm for 10 s. After this, the optical clarity of the substrate was evaluated using the NBS-1952 Resolution Test Chart and the performance was recorded on video with a cell phone camera.

7. Procedure for Durability Testing of Antifogging Films

   Films were coated onto substrates, as previously mentioned. A gloved hand or a Kimtech Kimwipe were the media used to test abrasion resistance. Three to five abrasions would be applied to the film-coated substrate. The surface of the substrate would then be inspected for visible damage and the substrate would be evaluated for antifogging ability as described above.

8. Method for Kinetics Study via UV-Vis Spectroscopy:

   Isobutyl-modified quartz slides (AdValue Technology) were coated with polymer solution to make a uniform film (either drop-casting or spin-coating). Then, the slides were exposed to UV radiation for a predefined time (ranging from 10 s to 20 min). The UV absorbance was measured at the wavelength corresponding to the ketone structure (which turns into an alcohol upon crosslinking) to monitor the kinetics of the crosslinking reaction.

Results and Discussion

Initially, the processes outlined above allowed for the synthesis, application, and curing of robust antifogging thin films based on the BPMPC copolymer shown in Figure 1. Samples were collected and sent to DEVCOM Soldier Center for evaluation.

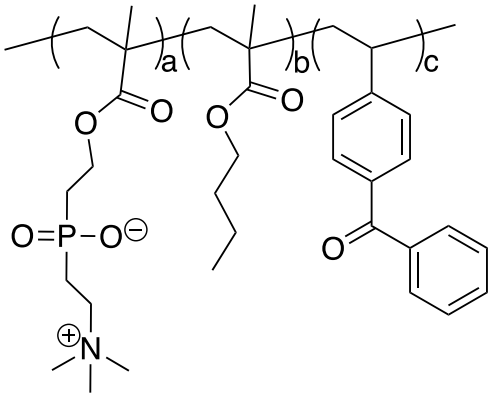

Figure 1. BPMPC Copolymer

This polymer was synthesized according to the project team's previous work [41] and was applied to a variety of substrates. Antifogging was successful and durable on isobutyl-modified glass slides as shown in Figure 2.

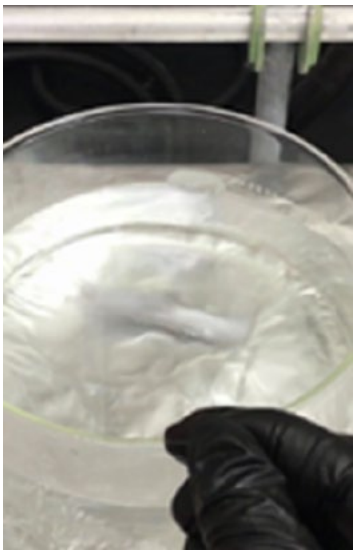

Figure 2. BPMPC copolymer coated and cured on isobutyl-modified glass slide. The clarity of the slide demonstrates the antifogging ability when held over hot water.

Polycarbonate goggle lenses were also tested. The lenses provided already had an antifogging coating applied, so this was first removed with ethanol washes, and the removal was confirmed with ATR-FTIR. The disappearance of the peaks at 1730 cm^{-1}, 1125 cm^{-1} and 1245 cm^{-1} are all evidence of the original coating being fully removed, as shown in Figure 3.

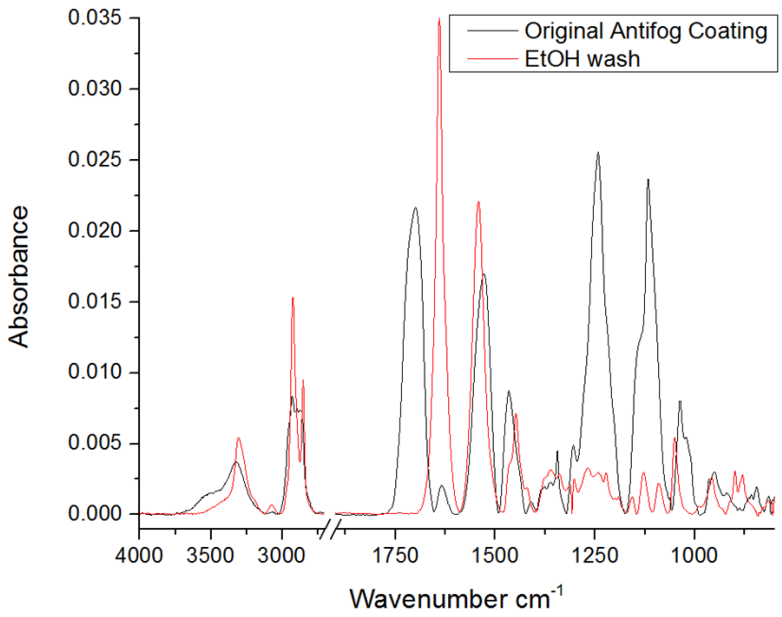

Figure 3. ATR-FTIR Spectra of goggles before and after factory antifog coating was removed

After the coating was removed, the BPMPC coating could be applied and the coating UV-cured, resulting in durable antifogging coatings, as seen in Figure 4.

Figure 4. BPMPC copolymer applied and cured on WileyX lens, which had the factory antifog coating removed.

In early experiments, there was consistent and repeatable success in synthesizing and curing this high-performance antifogging copolymer. However, after the initial successes, the technology's performance was suddenly unable to be replicated. The reasons for the

sudden lack of performance are still unknown, but a variety of troubleshooting routes have been employed to elucidate the cause.

A. Troubleshooting the 4-Vinylbenzophenone Monomer

The lack of performance that UGA observed had two components. First, the antifogging behavior became almost nonexistent after UV irradiation, almost regardless of duration. Secondly, the durability of the crosslinked system was very poor. To solve the second issue, UGA investigated the 4-vinylbenzophenone (4-vBP) monomer by following the original synthesis as closely as records allowed. This included checking the starting materials for lot numbers and impurities. The published procedure allowed for relatively pure starting material; it was found that the durability of the system had not improved by any meaningful regard. To further troubleshoot this, UGA continued by making pure 4-vBP through a Denmark-Hiyama coupling. This procedure yielded the desired product in very high levels of purity, albeit through a rather expensive procedure comparatively. Even with the high level of purity, the desired performance was not achieved with regards to both durability and antifogging ability when incorporated into the BPMPC monomer.

B. Other Variations of Benzophenone Monomers

The project team also synthesized the benzophenone derivatives shown in Figure 5: benzophenone reverse ester (BPRE) and benzophenone ester (BPE) as reported in the project team's work.[41]

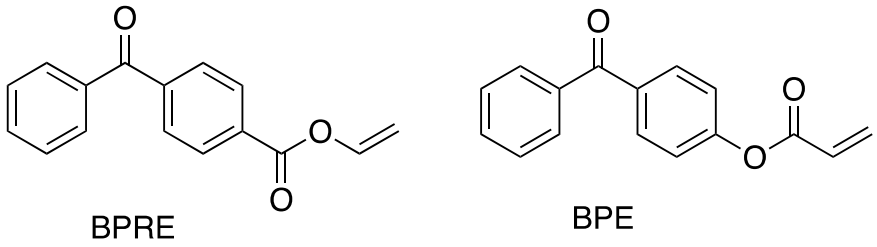

Figure 5. BPRE and BPE Esters synthesized in the work.

Both esters have been investigated for use in the BPMPC copolymer as a replacement for 4-vBP. The rates of crosslinking for each monomer (including 4-vBP) were studied and reported in work from UGA in 2020. Even though these crosslinkers should provide crosslinking, they did not allow for either the durability or the antifogging behavior required.

The project team also tried the anthraquinone-based crosslinker shown in Figure 6, which is used extensively by Rühe et al.,[42] and from which the rates of crosslinking have also been reported. This monomer was appealing because it could be crosslinked at 365 nm irradiation, which could minimize unknown side reactions from high-energy radiation.

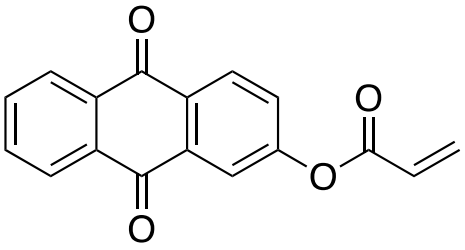

Figure 6. AOAQ Monomer

Incorporating this at 5 mol % (and other loadings) led to no significant results. Even irradiation at 365 nm for greater than 10 min led to no notable durability. For each of the monomers shown above, there is published data on the kinetics of the crosslinking reaction. Each monomer was tried at various concentrations (varied in series) to attempt to achieve acceptable performance without success.

C. Azide-Based Crosslinking Monomers

There are applications in the literature using azide-based crosslinkers based on the ability of UGA to evolve nitrogen gas, leaving behind a nitrene that can abstract hydrogen atoms to crosslink as shown in Figure 7. [43]

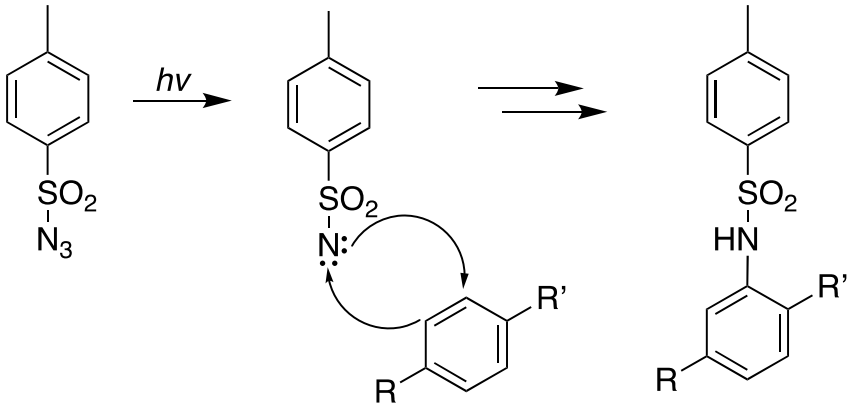

Figure 7. Photocrosslinking of sulfonyl nitrenes.

Because of this, UGA synthesized three azide-based monomers, shown in Figure 8, to evaluate their ability to crosslink when incorporated into an antifogging copolymer.

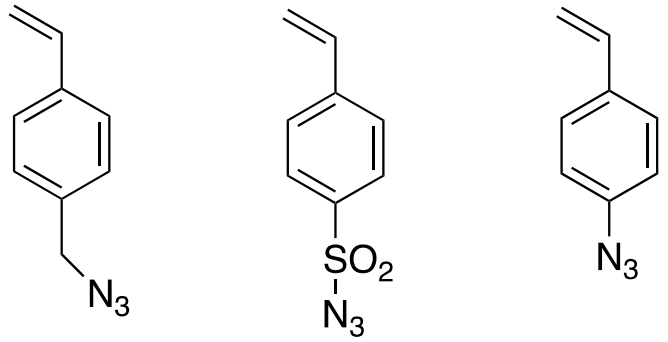

Figure 8. From left to right: 4vBA, SsAz, and SAz

4-Vinyl benzyl azide (4vBA), styrene-sulfonyl azide (SsAz), and styrene azide (SAz) were synthesized and evaluated for their ability to crosslink an antifogging copolymer. However, none of the monomers, even at varied concentrations, allowed for meaningful durability. The antifogging ability of each copolymer was poor.

D. Troubleshooting Copolymer Composition

Much effort was dedicated to investigating the copolymer composition, which encompasses multiple parts:

i. Variation of Acrylate Comonomer

The acrylate comonomers (n-butyl methacrylate (n-BuMA) and isobutyl methacryalate (i-BMA) were used in varying ratios between 10%-30%. These comonomers allowed for increased hydrophobicity of the antifogging thin film while also providing aliphatic carbon chains for crosslinking to occur.

ii. Variation of Antifogging Component:

The zwitterionic MPC comonomer was substituted with two other common antifogging agents. First, sulfobetaine methacrylate (SBMA) was tried. However, this copolymerization was not accomplished in any solvent system that UGA tried besides completely aqueous. UGA also tried polyethylene glycol methacrylate (PEG-MA) as an antifogging component. However, the durability of these copolymers was remarkably poor.

iii. Variation of Initiator:

The amount of initiator used for the original crosslinking studies was ambiguous. Because of this, both 0.5 mol% and 1 mol % of AIBN initiator were used with most formulations to ensure maximum molecular weight.

iv. Purity of Polymerization Components:

AIBN was used both as received (this is reported in UGA's original work) and freshly recrystallized. The monomers had inhibitor in them that was trialed with it both removed and kept in the monomer.

v. Variation of Polymer Ratios

Each of the comonomers were systematically varied to try and optimize the copolymer composition. The polymerizations were done in groups and the products irradiated for varying durations, ranging from 10 s to 20 min. An array of polymers synthesized is shown in Table 1. The table shows variations in each monomer ratio, as well as the concentration of the polymerization.

Table 1. Comonomer variations of BPMPC copolymers

Blend	**% MPC:**	**% i-BMA:**	**% 4-vBP:**	**Concentration:**
1	70	30	0	1M
2	70	27.5	2.5	1M
3	70	25	5	1M
4	70	22.5	7.5	1M
5	70	20	10	1M
6	70	27.5	2.5	0.5M
7	70	25	5	0.5M
8	70	22.5	7.5	0.5M
9	70	20	10	0.5M

After each of these variations, the products were spin coated onto polycarbonate and glass slides, irradiated, and evaluated for antifogging and durability. However, none of the combinations above offered any meaningful antifogging ability or durability.

E. Varying Polymerization Conditions

Various conditions for the polymerizations were attempted, specifically varying the solvents and the temperature of the reaction. The solvents include 200 proof ethanol, reagent alcohol, ethyl acetate, toluene, acetonitrile, and water. Temperatures were either 60 °C or 65 °C. The conditions are outlined in Table 2.

Table 2. Summary of solvent and heating conditions evaluated for the synthesis of antifogging copolymers.

Solvent System:	**Temperature:**
200 Proof Ethanol	60 °C and 65 °C
Reagent Alcohol (VWR)	60 °C and 65 °C
Toluene	65 °C
1:1 Ethyl Acetate / Toluene	65 °C
1:1 Ethanol/Water	65 °C
Acetonitrile	65 °C
Water	65 °C

F. Substrate Variation

Many substrates were tried, but primarily the focus was on using isobutyl-modified glass slides and polycarbonate. Isobutyl-modified glass was preferred because of a large percentage of easily-abstractable hydrogen atoms on the surface of the glass. Polycarbonate was the desired substrate for final application. Other substrates attempted include polyethylene, polystyrene, and polypropylene.

G. Analysis of Surfaces

The surfaces, both pre- and post-treatment, were analyzed with AFM to confirm that the topography was consistent with a smooth thin film as shown in Figure 9 below.

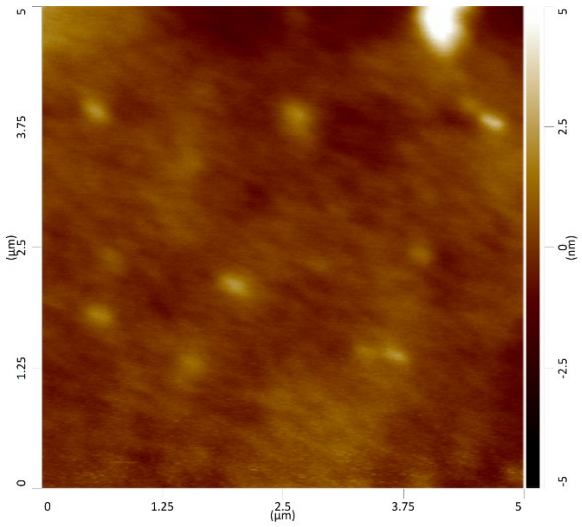

Figure 9. Tapping-Mode AFM Image of UV-cured antifogging thin film

The presence of the antifogging thin film was further confirmed with ATR-FTIR and Drop Shape Analysis (DSA). Thickness of the films was measured with AFM and spectroscopic ellipsometry. In each case, the results were optimized to be consistent with the results from when the technology worked as intended.

Each of the above troubleshooting options were investigated in many combinations. However, even with the large number of options, the desired performance for the antifogging copolymer was not achieved.

Conclusions

This study included a significant amount of troubleshooting in an attempt to reproduce successful antifogging technology. A multitude of routes were explored, each returning inconsistent results, which can be attributed to either impurity in the materials, surface aggregation phenomenon, improper film forming ability, reduced molecular weight, or other unknown factors. However, it was found that there are many possible crosslinking agents that could be applied to other copolymer systems. 4-vBP, BPRE, BPE, and AOAQ all have crosslinking kinetics that are thoroughly explored in this project and other literature, and because of this, it is recommended that these comonomers be considered for applications where photocrosslinking is required. Durable antimicrobial coatings, antifouling, lubricating, robust hardness, and multifunctional surfaces all are applications where photocrosslinking and grafting can play an important role in the future.

This document reports research undertaken at the U.S. Army Combat Capabilities Development Command Soldier Center, Natick, MA, and has been assigned No. Natick/TR-24/006 in a series of reports approved for publication.

References

1. Zhao, J.; Meyer, A.; Ma, L.; Wang, X. J.; Ming, W. H., Terpolymer-based SIPN Coating With Excellent Antifogging and Frost-resisting Properties. RSC Adv. 2015, 5, 102560-102566.
2. Chevallier, P.; Turgeon, S.; Sarra-Bournet, C.; Turcotte, R.; Laroche, G., Characterization of Multilayer Anti-Fog Coatings. Acs Appl Mater Inter 2011, 3, 750-758.
3. Petit, J.; Bonaccurso, E., General Frost Growth Mechanism on Solid Substrates with Different Stiffness. Langmuir 2014, 30, 1160-1168.
4. Wang, Y.; Li, T. Q.; Li, S. H.; Sun, J. Q., Antifogging and Frost-Resisting Polyelectrolyte Coatings Capable of Healing Scratches and Restoring Transparency. Chem. Mater. 2015, 27, 8058-8065.
5. Howarter, J. A.; Youngblood, J. P., Self-Cleaning and Next Generation Anti-Fog Surfaces and Coatings. Macromol. Rapid Commun. 2008, 29, 455-466.
6. Watanabe, T.; Nakajima, A.; Wang, R.; Minabe, M.; Koizumi, S.; Fujishima, A.; Hashimato, K., Photocatalytic Activity and Photoinduced Hydrophilicity of Titanium Dioxide Coated Glass. 2nd International Conference on Coatings on Glass, Iccg 1999, 374-377.
7. Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kojima, E.; Kitamura, A.; Shimohigoshi, M.; Watanabe, T., Light-induced Amphiphilic Surfaces. Nature 1997, 388, 431- 432.
8. Fujishima, A.; Zhang, X. T.; Tryk, D. A., TiO2 Photocatalysis and Related Surface Phenomena. Surf. Sci. Rep. 2008, 63, 515-582.
9. Lai, Y. K.; Tang, Y. X.; Gong, J. J.; Gong, D. G.; Chi, L. F.; Lin, C. J.; Chen, Z., Transparent Superhydrophobic/Superhydrophilic TiO2-based Coatings for Self-cleaning and Antifogging. J. Mater. Chem. 2012, 22, 7420-7426. 99
10. Zhang, L. B.; Li, Y.; Sun, J. Q.; Shen, J. C., Mechanically Stable Antireflection and Antifogging Coatings Fabricated by The Layer-by-layer Deposition Process and Postcalcination. Langmuir 2008, 24, 10851-10857.
11. de Leon, A.; Advincula, R. C., Reversible Superhydrophilicity and Superhydrophobicity on a Lotus-Leaf Pattern. Acs Appl Mater Inter 2014, 6, 22666-22672.
12. Raza, A.; Ding, B.; Zainab, G.; El-Newehy, M.; Al-Deyab, S. S.; Yu, J. Y., In situ Crosslinked Superwetting Nanofibrous Membranes for Ultrafast Oil-water Separation. J. Mater. Chem. A 2014, 2, 10137-10145.
13. Zhang, L.; Zhao, N.; Xu, J., Fabrication and Application of Superhydrophilic Surfaces: A Review. J. Adhes. Sci. Technol. 2014, 28, 769-790.
14. Liang, T.; Li, H.; Lai, X.; Su, X.; Zhang, L.; Zeng, X., A Facile Approach to UV-curable Super-hydrophilic Polyacrylate Coating Film Grafted on Glass Substrate. J. Coat. Technol. Res. 2016, 13, 1115-1121.
15. Ezzat, M.; Huang, C., Zwitterionic Polymerbrush Coatings with Excellent Anti-fog and Anti-frost Properties. RSC Adv. 2016, 6, 61695-61702.
16. Wolpers, A.; Vana, P., UV Light as External Switch and Boost of Molar-Mass Control in Iodine-Mediated Polymerization. Macromolecules 2014, 47, 954-963.

17. Ge, J. P.; Lee, H.; He, L.; Kim, J.; Lu, Z. D.; Kim, H.; Goebl, J.; Kwon, S.; Yin, Y. D., Magnetochromatic Microspheres: Rotating Photonic Crystals. J. Am. Chem. Soc. 2009, 131, 15687-15694.
18. Brown, P. S.; Atkinson, O. D.; Badyal, J. P., Ultrafast Oleophobic-hydrophilic Switching Surfaces for Antifogging, Self-cleaning, and Oil-water Separation. Acs Appl Mater Inter 2014, 6, 7504-11. 100
19. Hyomin Lee, M. L. A., Michael F. Rubner, Robert E. Cohen, Zwitter-Wettability and Antifogging Coatings with Frost-Resisting Capabilities. ACS Nano 2013, 7, 2172-2185. 20. Howarter, J. A.; Youngblood, J. P., Self-Cleaning and Anti-Fog Surfaces via StimuliResponsive Polymer Brushes. Adv. Mater. 2007, 19, 3838-3843.
21. Zhang, Z.; Chen, S. F.; Chang, Y.; Jiang, S. Y., Surface Grafted Sulfobetaine Polymers via Atom Transfer Radical Polymerization as Superlow Fouling Coatings. J. Phys. Chem. B 2006, 110, 10799-10804.
22. Liu, P. S.; Domingue, E.; Ayers, D. C.; Song, J., Modification of Ti6Al4V Substrates with Well-defined Zwitterionic Polysulfobetaine Brushes for Improved Surface Mineralization. Acs Appl Mater Inter 2014, 6, 7141-7152.
23. Singha, P.; Locklin, J.; Handa, H., A Review of The Recent Advances in Antimicrobial Coatings for Urinary Catheters. Acta Biomater. 2017, 50, 20-40.
24. Li, C.; Li, X.; Tao, C.; Ren, L.; Zhao, Y.; Bai, S.; Yuan, X., Amphiphilic Antifogging/AntiIcing Coatings Containing POSS-PDMAEMA-b-PSBMA. Acs Appl Mater Inter 2017, 9, 22959- 22969.
25. Lin, X.; Fukazawa, K.; Ishihara, K., Photoreactive Polymers Bearing a Zwitterionic Phosphorylcholine Group for Surface Modification of Biomaterials. Acs Appl Mater Inter 2015, 7, 17489-98.
26. Ercole, F.; Davis, T. P.; Evans, R. A., Photo-responsive Systems and Biomaterials: Photochromic Polymers, Light-triggered Self-assembly, Surface Modification, Fluorescence Modulation and Beyond. Polym. Chem. 2010, 1, 37-54.
27. Dorman, G.; Prestwich, G. D., Benzophenone Photophores in Biochemistry. Biochemistry 1994, 33, 5661-5673. 101
28. Higuchi, H.; Yamashita, T.; Horie, K.; Mita, I., Photo-Cross-Linking Reaction of Benzophenone-Containing Polyimide and Its Model Compounds. Chem. Mater. 1991, 3, 188-194.
29. Toomey, R.; Freidank, D.; Ruhe, J., Swelling behavior of thin, surface-attached polymer networks. Macromolecules 2004, 37, 882-887.
30. Pahnke, J.; Ruhe, J., Attachment of Polymer Films to Aluminium Surfaces by Photochemically Active Monolayers of Phosphonic Acids. Macromol. Rapid Commun. 2004, 25, 1396-1401.
31. Shen, W. W.; Boxer, S. G.; Knoll, W.; Frank, C. W., Polymer-supported Lipid Bilayers on Benzophenone-modified Substrates. Biomacromolecules 2001, 2, 70-79. 32. Virkar, A.; Ling, M. M.; Locklin, J.; Bao, Z., Oligothiophene Based Organic Semiconductors with Cross-linkable Benzophenone Moieties. Synth. Met. 2008, 158, 958-963.
33. Samuel, J. D. J. S.; Brenner, T.; Prucker, O.; Grumann, M.; Ducree, J.; Zengerle, R.; Ruhe, J., Tailormade Microfluidic Devices Through Photochemical Surface Modification. Macromol. Chem. Phys. 2010, 211, 195-203.

34. Hu, S. W.; Ren, X. Q.; Bachman, M.; Sims, C. E.; Li, G. P.; Allbritton, N. L., Surfacedirected, Graft Polymerization within Microfluidic Channels. Anal. Chem. 2004, 76, 1865-1870.
35. Prucker, O.; Brandstetter, T.; Ruhe, J., Surface-attached Hydrogel Coatings via C-H insertion Crosslinking for Biomedical and Bioanalytical Applications (Review). Biointerphases 2018, 13.
36. Abu-Rabeah, K.; Atias, D.; Herrmann, S.; Frenkel, J.; Tavor, D.; Cosnier, S.; Marks, R. S., Characterization of Electrogenerated Polypyrrole-Benzophenone Films Coated on Poly(pyrrolemethyl metacrylate) Optic-Conductive Fibers. Langmuir 2009, 25, 10384-10389. 102 37. Brandstetter, T.; Bohmer, S.; Prucker, O.; Bisse, E.; zur Hausen, A.; Alt-Morbe, J.; Ruhe, J., A Polymer-based DNA Biochip Platform for Human Papilloma Virus Genotyping. J. Virol. Methods 2010, 163, 40-48.
38. Yatvin, J.; Gao, J.; Locklin, J., Durable Defense: Robust and Varied Attachment of Nonleaching Poly"-onium" Bactericidal Coatings to Reactive and Inert Surfaces. Chem. Commun. 2014, 50, 9433-9442.
39. Gao, J.; Martin, A.; Yatvin, J.; White, E.; Locklin, J., Permanently Grafted Icephobic Nanocomposites with High Abrasion Resistance. J. Mater. Chem. A 2016, 4, 11719-11728.
40. Liu, Q. H.; Singha, P.; Handa, H.; Locklin, J., Covalent Grafting of Antifouling Phosphorylcholine-Based Copolymers with Antimicrobial Nitric Oxide Releasing Polymers to Enhance Infection-Resistant Properties of Medical Device Coatings. Langmuir 2017, 33, 13105- 13113.
41. Liu, Q.; Locklin, J. L. Photocross-Linking Kinetics Study of Benzophenone Containing Zwitterionic Copolymers. *ACS Omega* **2020**, *5* (16), 9204–9211.
42. Straub, A. J.; Scherag, F. D.; Kim, H. I.; Steiner, M.-S.; Brandstetter, T.; Rühe, J. “Chicable” and “Clickable” Copolymers for Network Formation and Surface Modification. *Langmuir* **2021**, *37* (21), 6510–6520.
43. Yatvin, J.; Sherman, S. A.; Filocamo, S. F.; Locklin, J. Direct Functionalization of Kevlar® with Copolymers Containing Sulfonyl Nitrenes. *Polymer Chemistry* **2015**, *6* (16), 3090–3097.

List of Acronyms

AFM	Atomic Force Microscopy
AOAQ	Acryloyloxyanthraquinone
ATR-FTIR	Attenuated Total Reflection Fourier-Transform Infrared Spectroscopy
BP	Benzophenone
BPE	Benzophenone Ester
BPMPC	2-methacryloyloxyethyl phosphorylcholine-co-butyl methacrylate-co-benzophenone
BPRE	Benzophenone Reverse Ester
DSA	Drop Shape Analysis
^{1}H NMR	Proton (^{1}H) Nuclear Magnetic Resonance
i-BMA	Isobutyl Methacrylate
i-BTS	Isobutyl Trichlorosilane
n-BuMA	n-Butyl Methacrylate
MPC	2-Methacryloyloxyethyl Phosphorylcholine
SAz	4-Azidostyrene
SsAz	4-Styrene Sulfonyl Azide
SBMA	Sulfobetaine Methacrylate
TiO_2	Titanium Dioxide
UV	Ultraviolet
4-vBP	4-Vinylbenzophenone
4-vBA	4-Vinyl Benzyl Azide
ZnO	Zinc Oxide