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Antibacterial Polymer Coatings

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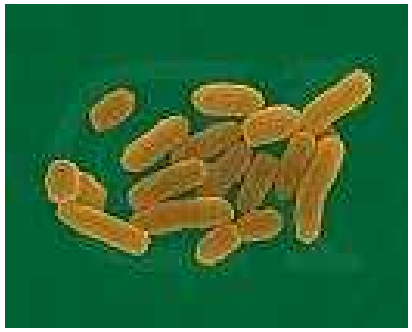
The Problem: Develop a Self-Decontaminating Coating that Kills Microorganisms on Contact in the Event of a Biological Attack

Technical Challenges:

1) Coating should be easy to apply (spray-on).
2) Coating should be durable.
3) Coating should kill a wide variety of microorganisms.
4) Active and/or toxic agents should not leach out of coating.

viruses (smallpox)[1]



vegetative bacteria (plague)[2]

spores (anthrax)[3]

[1] CDC/ Dr. Fred Murphy, Sylvia Whitfield
[2] Dennis Kunkel Microscopy, Inc.
[3] www.srs.dl.ac.uk/Annual_Reports/AnRep01_02/anthrax.htm

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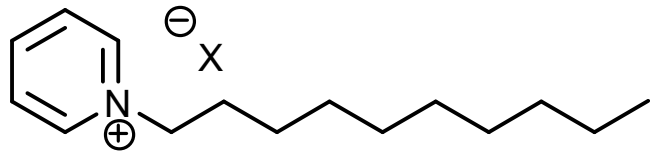
Quaternary Ammonium Compounds (QACs) as Antibacterial Agents

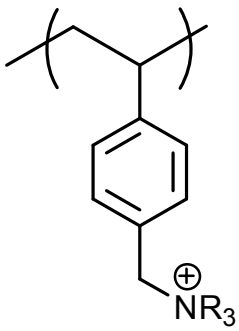
Mode of action:



1) Positive charge promotes electrostatic interaction with negatively charged cell surface

2) Lipophilic chain promotes diffusion into and/or through the cell wall

Previous Work with QACs on polymers:



- Polymers exhibited higher antimicrobial activities than corresponding low molecular weight model compounds.[1]
- QACs acting in concert are more effective than individual molecules.
- These polymers were all water soluble.

[1] Ikeda, I.; Tazuke, S.; Suzuki, Y. *Makromol. Chem*. **1984**, 185, 869.

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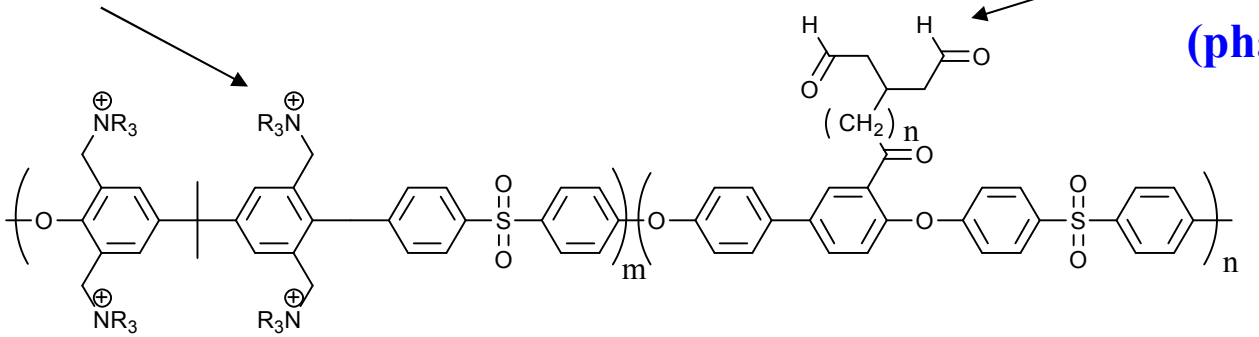
Approach:

Polymer has quaternary ammonium groups to kill bacteria…

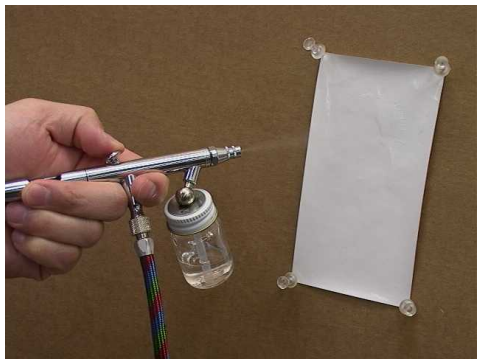
(phase 1)

…and pendant aldehydes to kill spores

(phase 2)



Polymers can be dissolved in mixtures of water and alcohol,



sprayed onto various surfaces,

and tested for biocidal activity

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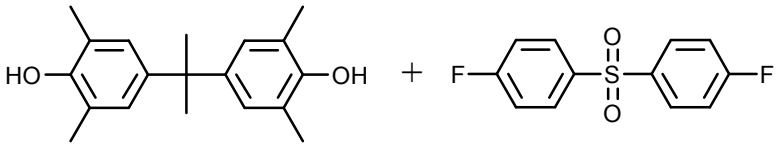
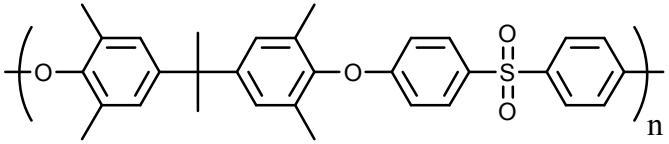
Synthesis of Sandia QA Polymer

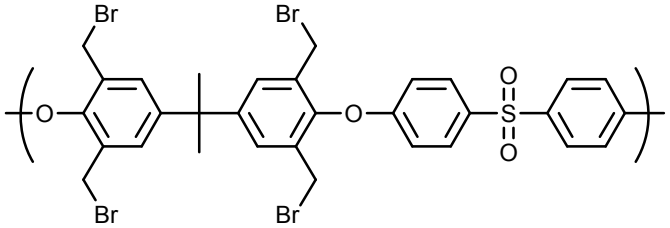


K_2CO_3, NMP
175 °C, 24 h



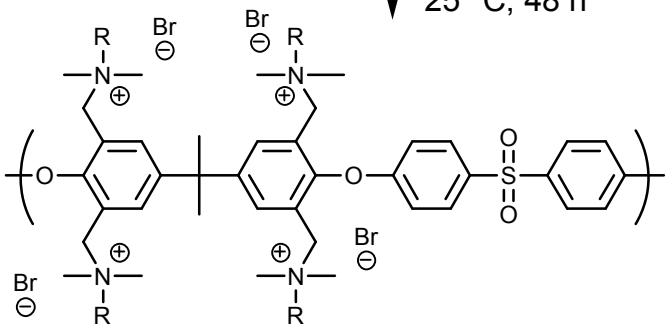
M_w = 70-110k

NBS, benzoyl peroxide
80 °C, 3 h



Note: not all methyl groups are converted to CH_2Br

$NR(CH_3)_2$, DMAc
25 °C, 48 h



R = CH_3, $(CH_2)_7CH_3$, $(CH_2)_9CH_3$, $(CH_2)_{11}CH_3$, or $(CH_2)_{13}CH_3$

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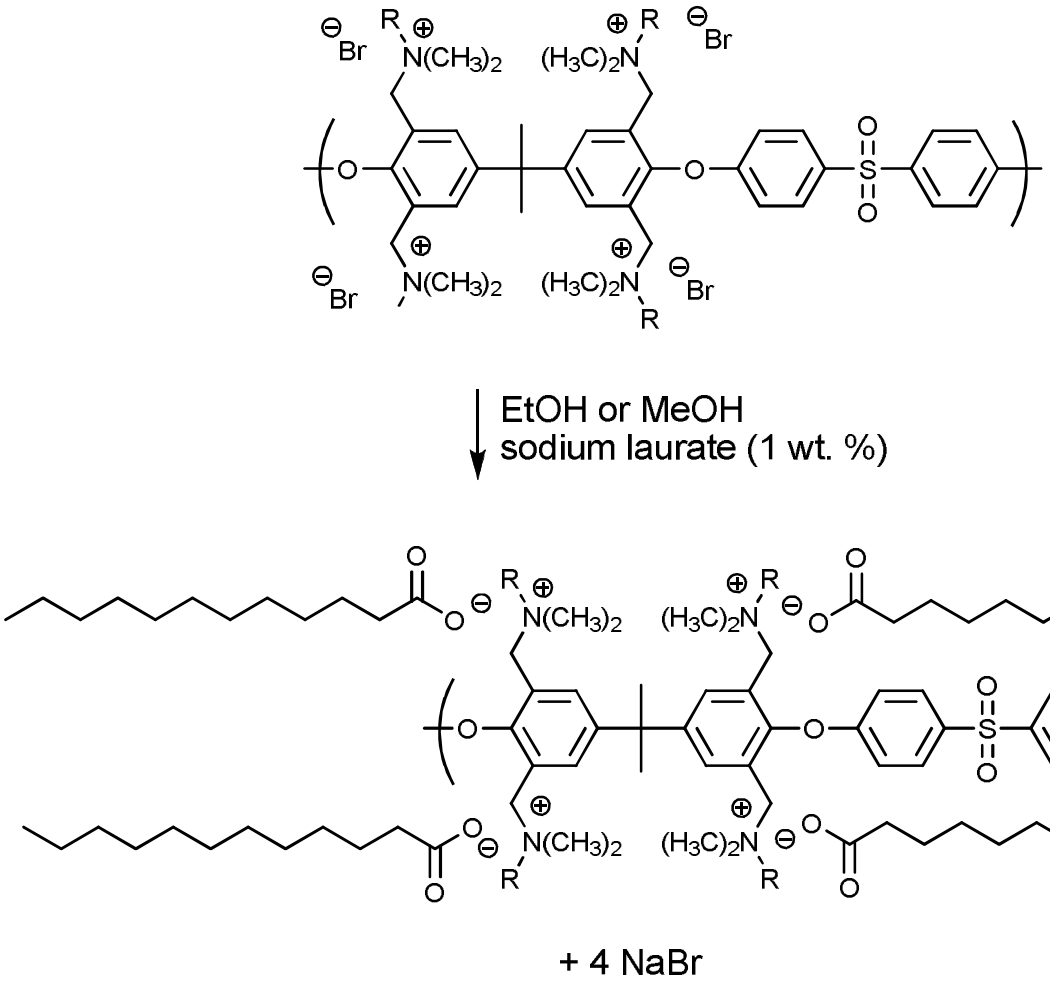
Making Polymer Solutions



- Br^- form polymers are only slightly soluble in polar aprotic solvents.
- Laurate form polymers dissolve in alcohols to make 1-3 wt. % solutions.

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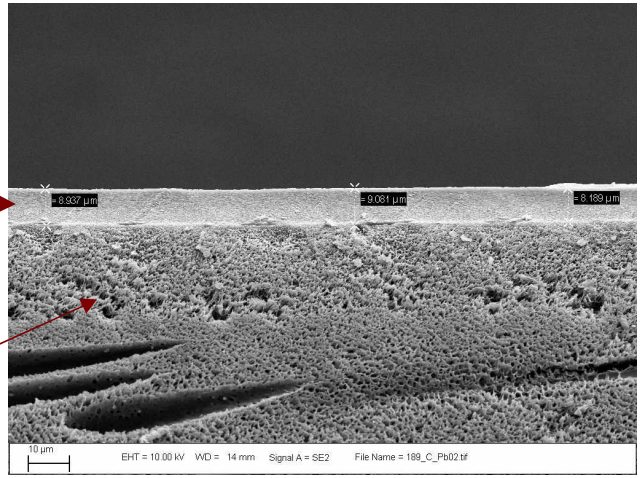
Spraying and Testing

Spraying on coating

Dense polymer coating, 5-10 microns thick

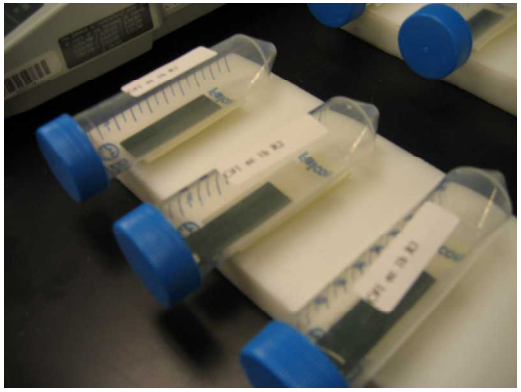
Porous substrate



SEM of cross-section

Biological Testing:

Testing set-up



CARC-coated coupons

Sample plating

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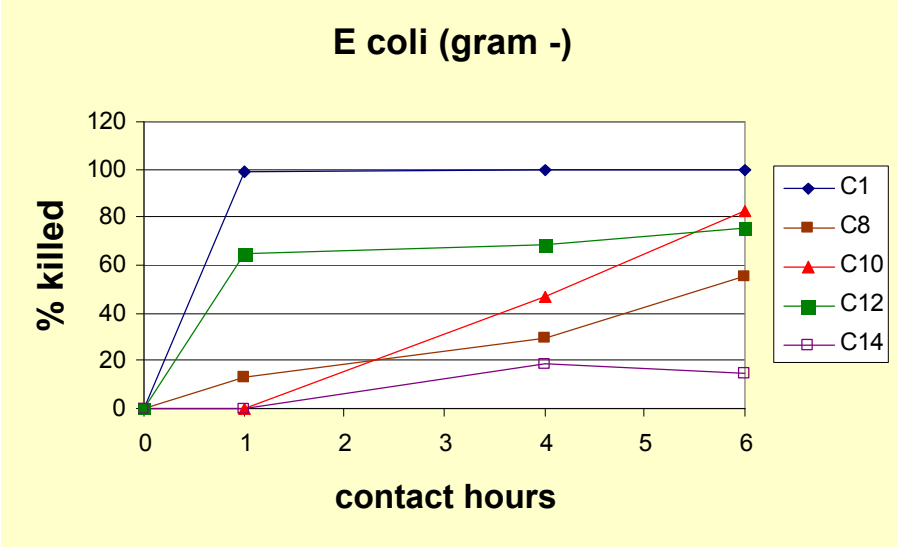
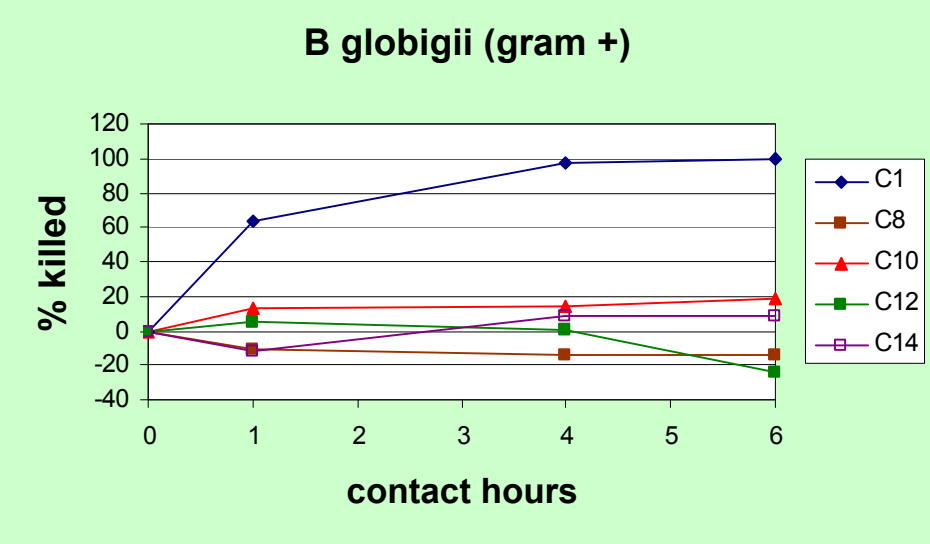
Effect of Alkyl Chain Length

% of organisms killed on coated surface vs. CARC control surface





- The coating with the one-carbon alkyl chain is the most effective against both organisms.
- The gram negative bacterium is easier to kill than the gram positive one.
- The C1 coating is the most hydrophilic, so aqueous samples spread out more, leading to more intimate contact.

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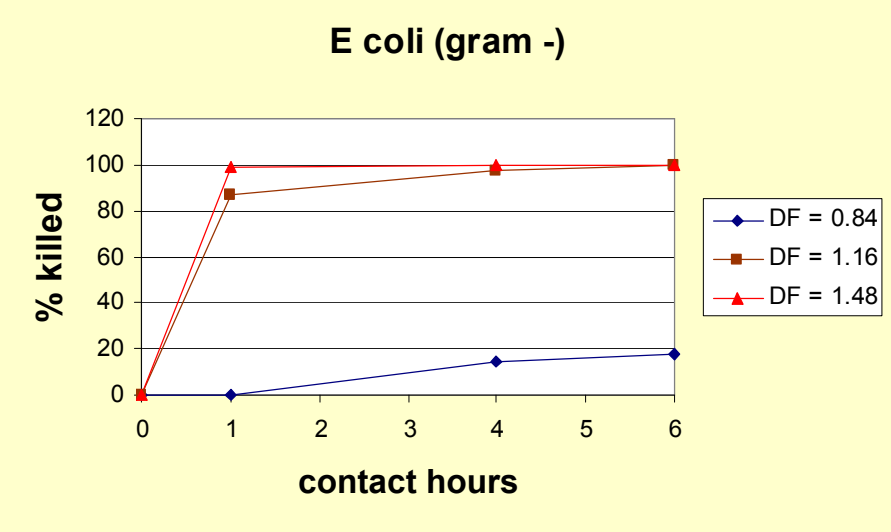
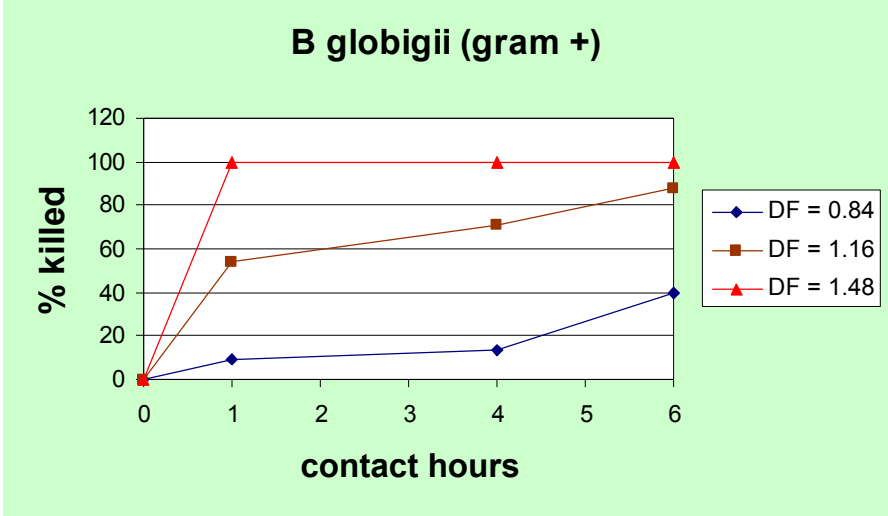
Effect of Density of QA Groups

% of organisms killed on coated surface vs. CARC control surface





- R = C1 (methyl).
- DF (Degree of Functionality) = Number of QA groups per polymer repeat unit.
- Polymers with DF > 1.48 are soluble in water (unusable).
- As expected, coatings with greater DF values are more effective against both organisms.

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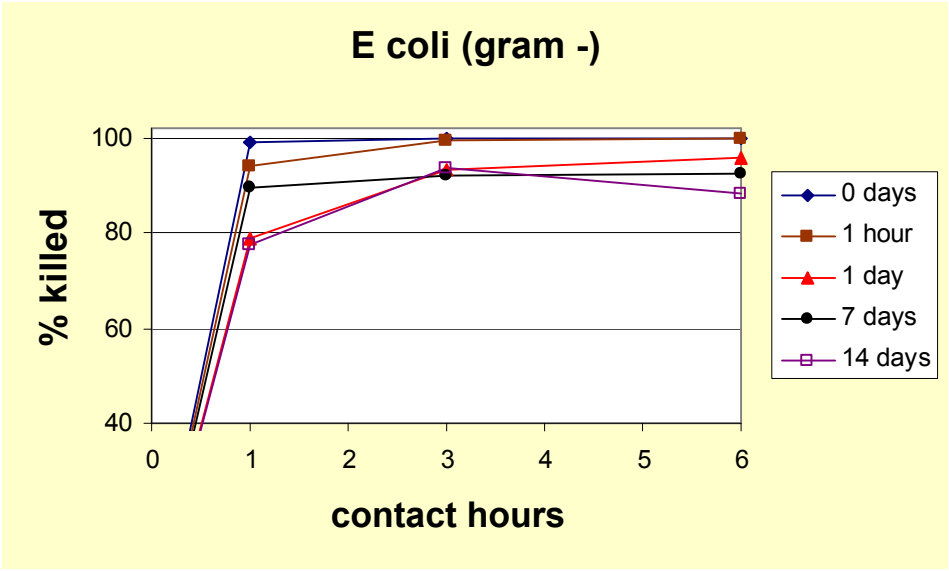
Durability in Water

Coated samples in water durability test

% of organisms killed on coated surface vs. CARC control surface



- Sample coupons were immersed in deionized water at 25 °C and were gently swirled for up to 14 days to see if coatings would wash off.
- Coating still kills > 80 % of E. coli after 14 days in water, although effectiveness does decrease with exposure to water.

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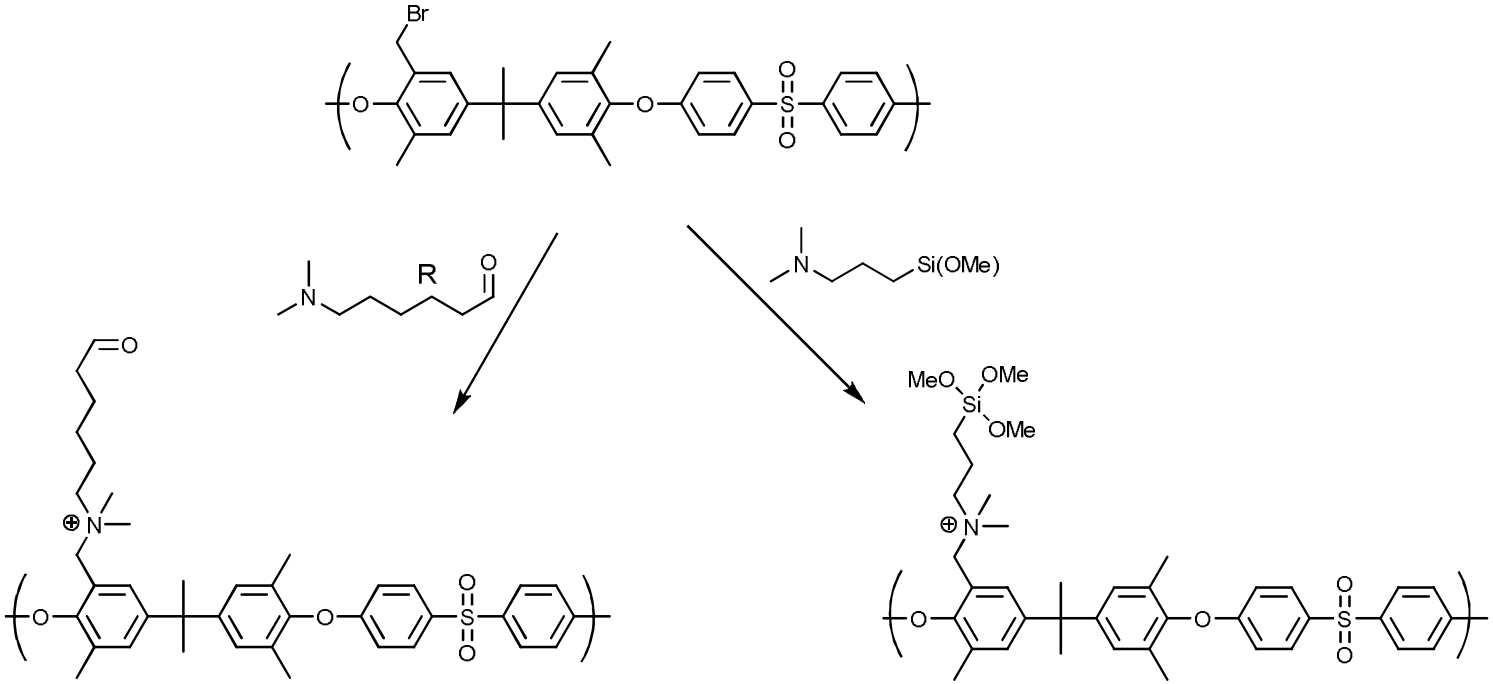
Conclusions

- A series of poly(sulfones) with various quaternary ammonium groups has been synthesized.
- The ionomers can be rendered soluble in alcohols by exchanging in laurate anions and the ionomer solutions can be applied as coatings by spraying.
- All of the coatings show some biotoxicity but the C1 coating is clearly the most effective against both vegetative bacteria tested.
- Effectiveness increases with higher density of QA groups.
- Effectiveness decreases slightly with water washing but C1 coating does not wash off.
- Aldehyde groups will be added to give sporicidal activity.

Next Steps



QA polymer with pendant aldehyde

QA polymer with pendant trimethoxy silane

- Aldehydes should add sporicidal activity.
- Trimethoxy silane groups can react with OH groups on surfaces (glass, cotton, metals) to bond coatings.
- Durability of coatings to heat and UV exposure needs to be tested.

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Acknowledgements

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