Synthesis, Mobility Study and Antimicrobial Evaluation of Novel Self-Spreading Ionic Silicone Oligomers

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ABSTRACT: Polydimethylsiloxanes (PDMS) have been extensively utilized for their ability to spread and lubricate surfaces. This ability can be mostly attributed to their low surface energy and extremely flexible backbone. This study examines their unique ability through a comparative analysis of the rates of spread of numerous commercially available oils and lubricants, including a series of methyl-terminated PDMS. The analysis facilitated the design and synthesis of two homologous series of PDMS, in which the terminal ends were functionalized as quaternary ammonium salts. The two new series of compounds were examined for their ability to spread both as neat liquids and as formulated blends. Additionally, these hybrid ionic oligomers were screened for biological activity against *Staphylococcus aureus*. All of the new oligomers exhibited antimicrobial properties in preliminary testing. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2954–2964, 2007

Key words: silicone; oligomers; biomaterials; amphiphiles; self-spreading

INTRODUCTION

The ability to disinfect surfaces and manufacture self-decontaminating surfaces is an area of research that has received much attention in recent years.[1–3] Applications for such products include hospital surfaces, medical implants, children's toys,[4,5] public transportation surfaces, and food preparation areas.[6,7] Although many of these surfaces can be cleaned through the use of topical disinfectants, the ability to continuously self-disinfect is particularly desirable with respect to long term maintenance costs associated with repeated topical surface disinfection. Furthermore, the ability to disinfect surfaces that cannot be easily accessed would be extremely advantageous from an economic standpoint.

Polydimethylsiloxanes (PDMS) have been used in many applications as a result of their commercial availability and physical properties such as low surface energy and versatility in wetting a variety of surfaces.[8] Moreover, a significant amount of attention has recently been directed toward the development of a novel class of PDMS-based biocides due to increased potential for microbial contamination and infectious risks to military personal and the general public.[9] In a recent study, Baney and coworkers[9] have demonstrated a unique class of biocides based on simple silicone chemistry derived from silanol intermediates. The silanols exhibited activity against both Gram-negative and Gram-positive bacteria and are considered environmentally benign.

In another report, quaternary ammonium silane-based biocides were used to coat silicone rubber shunt prosthesis, yielding a positively charged, antimicrobial surface.[10] The antimicrobial properties of positively-charged surface treatments are discussed in the context of multiorganism containing biofilms. Although the biocidal effect observed with this treatment could not be directly attributed to the positively charged surface, the study provides useful insights for applications where multiorganism biofilms present a risk for infection.

In another report, Carr et al.[11] described a novel aqueous biocide system composed of a water-soluble biocide and a polyorganosiloxane. The two components are combined and sprayed onto hard surfaces for disinfecting. The biocide is slowly released upon contact with water after drying on the deposited surface. Although a unique approach, the method lacks utility with respect to the decontamination of inaccessible surfaces and surfaces with preexisting contamination.

Work to formulate reloadable antimicrobial coatings based on amphiphilic silicone networks has been reported,[12] in which a thin, covalently, surface-attached

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coating was applied. Both hydrophobic and hydrophilic surfaces are present and demonstrate nanophase morphology. These coatings have shown antimicrobial activity against the bacterium *Staphylococcus aureus*, even after washing. This works appears promising; however, a major drawback of the method is that the coatings are difficult to apply to surfaces.

Hathorne et al.,[13] likewise, reported a study of latex degradation by microbial action. The focus was to determine how the structure and morphology of surfactants with ionic and nonionic end groups impact the efficacy of several biocides. The surfaces were successfully evaluated against *Pseudomonas aeruginosa* and *Escherichia coli*. Autoclaving and heating the material had a great impact on the efficacy of the performance.[13] This approach demonstrates that the degradation of latex by bacteria is frequently avoided; however, it does not demonstrate self-disinfection of the surface and ultimately requires heat activation.

Polyquaternary ammonium compounds have been prepared and evaluated as microbiocides, corrosion inhibitors, debonding agents, flocculants, softeners, antistatic agents, and demulsifiers.[14] Although successful in the described applications, these molecules are not mobile or self-spreading. Polysiloxanes bearing both primary alcohols and quaternary ammonium salts were incorporated in polyurethane films. Because the polyquats were covalently bound to the resin system, they were effective in place, yet lacked mobility.[15] Similarly, the preparation of biocide-incorporated silicone coatings for antifouling/foul release applications also has been investigated by numerous groups.[16] One group in particular has been successful in the synthesis of commercial biocides as alkyl moieties onto silicone backbones through covalent bonding and combinatorial schemes.[17,18] Synthetic control over the incorporation of crosslink functionalities within the polymer resin allowed tuning of the surface, the coating, and mechanical properties. Resistance to macrofouling was tested by static immersion tests, and preliminary results showed that the coatings prepared from biocide-incorporated silicones with the appropriate bulk modulus significantly reduced macrofouling. Silicone elastomers have also been used in many antifouling applications.[16] Their low surface energy and smooth surface is thought to weaken or eliminate the adhesive bond between fouling organisms and the coating, thereby allowing ships to be cleaned as they move.

In our laboratory, we wish to selectively incorporate many of the aforementioned properties to create a novel, self-spreading liquid that will decontaminate as it spreads over a variety of surfaces. We wish to take advantage of the antimicrobial properties of quaternary ammonium salts, as well as the low surface energy and flexible backbone that PDMS are known to possess. The strategy of this work is aimed at covalently bonding the antimicrobial moiety to the backbone affording the ability to self-spread and wet a variety of surfaces. The newly synthesized compounds will be able to spread into inaccessible locations while providing both immediate and persistent disinfection of the coated surfaces.

EXPERIMENTAL

Materials

All chemicals used were reagent grade and were purchased and used without further purification. Moisture sensitive reactions were conducted in oven-dried glassware under a nitrogen atmosphere. Unless otherwise noted, ^{1}H and ^{13}C NMR were taken in $CDCl_3$ at 300 MHz with a TMS internal standard. Chemical shifts are reported in units downfield from TMS. Coupling constants, *J*, are reported in units of Hertz (Hz). All T_g data were recorded using standard DSC techniques and equipment. External elemental analyses were performed by Atlantic Microlab, Norcross, GA 30,091. Calculated percent elemental compositions were based on manufacturer's molecular weight range; albeit unknown as to the distribution. All new oligomers are reported within ±0.4%.

General procedure for the preparation of functionalized PDMS compounds (5a-f)

Into a 50-mL round bottom flask equipped with reflux condenser and magnetic stir bar were placed 2.0 mmol of primary diamino PDMS (**3**), 12.5 mmol of alkyl bromide (**4**), and 25 mL of methanol. The resulting solution was allowed to reflux for 18 h under nitrogen. An excess of alkyl halide was employed to facilitate the purification process. All solvent and unreacted alkyl halide (bp 37–215°C) were evaporated under reduced pressure to afford the desired product in acceptable purity for this study. When desired, trituration of the reaction product with ethyl ether afforded a purer product.

N,N,N-Triethyl-N-propyl ammonium bromide terminated polydimethylsiloxanes (5a)

FTIR: 3414, 2960, 2898, 2794, 1593, 1408, 1266, 1104, 1015 cm^{-1}. ^{1}H NMR ($CDCl_3$): 3.24–2.93 (m, 16H), 1.92–1.85 (m, 4H), 1.57–1.40 (m, 18H), 0.67–0.55 (m, 4H), 0.14–0.05 δ (m, 72H). A colorless viscous liquid was afforded in 70% yield. *Anal. Calcd. range*: C, 38.95–38.21; H, 8.77–8.70; N, 2.39–2.12. Found: C, 38.28; H, 8.32; N, 1.84.

N,N,N,N-Tetrapropyl ammonium bromide terminated polydimethylsiloxanes (5b)

FTIR: 3420, 2960, 2898, 2802, 1943, 1604, 1447, 1404, 1262, 1108, 1004 cm^{-1}. ^1H NMR ($CDCl_3$): 3.02–2.91 (m, 16H), 2.04–1.83 (m, 16H), 1.06 (t, 18H), 0.66–0.58 (m, 4H), 0.18–0.04 δ (m, 72H). A pale yellow waxy solid was afforded in 65% yield. *Anal. Calcd. range*: C, 42.07–41.05; H, 9.15–9.04; N, 2.23–1.99. Found: C, 41.75; H, 8.83; N, 1.75.

N,N,N-Tributyl-N-propyl ammonium bromide terminated polydimethylsiloxanes (5c)

FTIR: 3391, 2956, 2798, 1936, 1585, 1450, 1424, 1258, 1112, 1008 cm^{-1}. ^1H NMR ($CDCl_3$): 3.12–2.95 (m, 16H), 1.94–1.83 (m, 16H), 1.52–1.42 (q, 12H), 1.07–0.94(m, 18H), 0.65–0.60 (m, 4H), 0.20–0.14 δ (m, 72H). A colorless solid was afforded in 62% yield. *Anal. Calcd. range*: C, 44.81–43.57; H, 9.48–9.34; N, 2.09–1.88. Found: C, 43.72; H, 9.42; N, 1.58.

N,N,N-Tripentyl-N-propyl ammonium bromide terminated polydimethylsiloxanes (5 days)

FTIR: 3422, 2968, 2798, 1939, 1593, 1454, 1412, 1258, 1119, 1004 cm^{-1}. ^1H NMR ($CDCl_3$): 3.12–2.92 (m, 16H), 1.94–1.83 (m, 16H), 1.37 (m, 24H), 0.95–0.90 (m, 18H), 0.62–0.58 (m, 4H) 0.15–0.10 δ (m, 72H). A colorless solid was afforded in 61%. *Anal. Calcd. range*: C, 47.22–45.82; H, 9.77–9.61; N, 1.97–1.78. Found: C, 45.48; H, 9.50; N, 1.60.

N,N,N-Trihexyl-N-propyl ammonium bromide terminated polydimethylsiloxanes (5e)

FTIR: 3418, 2964, 2871, 2794, 1951, 1585, 1466, 1404, 1266, 1104, 1012 cm^{-1}. ^1H NMR ($CDCl_3$): 3.03–2.98 (m, 16H), 1.91–1.83 (m, 16H), 1.34 (m, 36H), 0.90–0.89 (m, 18H), 0.66–0.58 (m, 4H), 0.14–0.01 δ (m, 72H). A pale yellow waxy solid was afforded in 53% yield. *Anal. Calcd. range*: C, 49.36–47.84; H, 10.02–9.86; N, 1.86–1.69. Found: C, 47.67; H, 9.62; N, 1.92.

N,N,N-Trioctadecyl-N-propyl ammonium bromide terminated polydimethyl siloxanes (5f)

FTIR: 3426, 2956, 2925, 2852, 1939, 1593, 1466, 1412, 1269, 1096, 1019 cm^{-1}. ^1H NMR ($CDCl_3$): 2.99 (m, 16H), 2.15–1.94 (m, 16H), 1.33–1.23 (m, 180H), 0.88 (t, 18H), 0.21–0.01 δ (m, 72H). A pale yellow solid was afforded in 35% yield. *Anal. Calcd. range*: C, 63.91–62.15; H, 11.77–11.57; N, 1.11–1.05. Found: C, 63.59; H, 11.61; N, 1.16.

General procedure for the preparation of functionalized PDMS compounds (7a-f)

Into a 50-mL round bottom flask equipped with reflux condenser and magnetic stir bar were placed 2.0 mmol of secondary amino PDMS (**6**), 8.3 mmol of alkyl bromide (**4**), and 25 mL of methanol. The resulting solution was then allowed to reflux for 18 h under nitrogen. The solvent and excess unreacted alkyl bromide were evaporated under reduced pressure to afford the desired product that could be used without further purification. A purified product was obtained by trituration with ethyl ether.

N,N,N-Triethyl-N-isobutyl ammonium bromide terminated polydimethylsiloxanes (7a)

FTIR: 3414, 2960, 2898, 2794, 1593, 1408, 1266, 1104, 1015 cm^{-1}. ^1H NMR ($CDCl_3$): 3.18–3.06 (m, 12H), 2.87–2.72 (m, 4H), 2.17 (m, 2H), 1.42 (t, 18H), 1.03 (d, 6H), 0.60–0.50 (m, 4H), 0.14–0.01 δ (m, 66H). A colorless waxy solid was afforded in 86% yield. *Anal. Calcd. range*: C, 39.39–38.21; H, 8.81–8.70; N, 2.55–2.12. Found: C, 38.85; H, 8.76; N, 2.48.

N-Ethyl-N,N-dipropyl-N-isobutyl ammonium bromide terminated polydimethyl siloxanes (7b)

FTIR: 3395, 2964, 2790, 2513, 1589, 1454, 1416, 1254, 1104, 1019 cm^{-1}. ^1H NMR ($CDCl_3$): 2.98–2.78 (m, 12H), 2.60–2.52 (m, 4H), 2.15–2.11 (m, 2H), 1.51 (t, 6H), 1.43–1.34 (m, 8H), 1.27 (d, 6H), 1.13 (t, 12H), 0.66–0.61 (m, 4H), 0.12–0.01 δ (m, 66H). A pale yellow waxy solid was afforded in 62% yield. *Anal. Calcd. range*: C, 41.64–40.14; H, 9.08–8.93; N, 2.43–2.04. Found: C, 40.76; H, 9.02; N, 2.35.

N-Ethyl-N,N-dibutyl-N-isobutyl ammonium bromide terminated polydimethyl siloxanes (7c)

FTIR: 3433, 2960, 2779, 2679, 2521, 1943, 1593, 1462, 1412, 1263, 1119, 1008 cm^{-1}. ^1H NMR ($CDCl_3$): 3.21–3.02 (m, 12H), 2.89–2.74 (m, 4H), 2.30 (m, 2H), 1.53 (t, 6H), 1.21 (d, 6H), 1.02–0.93 (m, 12H), 0.62–0.57 (4H), 0.11–0.01 δ (m, 66H). A pale yellow waxy solid was afforded in 71% yield. *Anal. Calcd. range*: C, 43.68–41.92; H, 9.33–9.15; N, 2.32–1.96. Found: C, 42.23; H, 9.22; N, 2.09.

N-Ethyl-N,N-dipentyl-N-isobutyl ammonium bromide terminated polydimethyl siloxanes (7d)

FTIR: 3391, 2964, 2871, 2787, 1466, 1412, 1262, 1092, 1023 cm^{-1}. ^1H NMR ($CDCl_3$): 3.25–3.14 (m, 12H), 2.92–2.69 (m, 4H), 2.11–2.08 (m, 2H), 1.51(t, 6H), 1.37–1.26 (m, 24H), 1.28 (d, 6H), 0.98 (t, 12H), 0.66–0.62 (m, 4H), 0.21–0.05 δ (m, 66H). A pale yellow solid was afforded in 68% yield. *Anal. Calcd. range*:

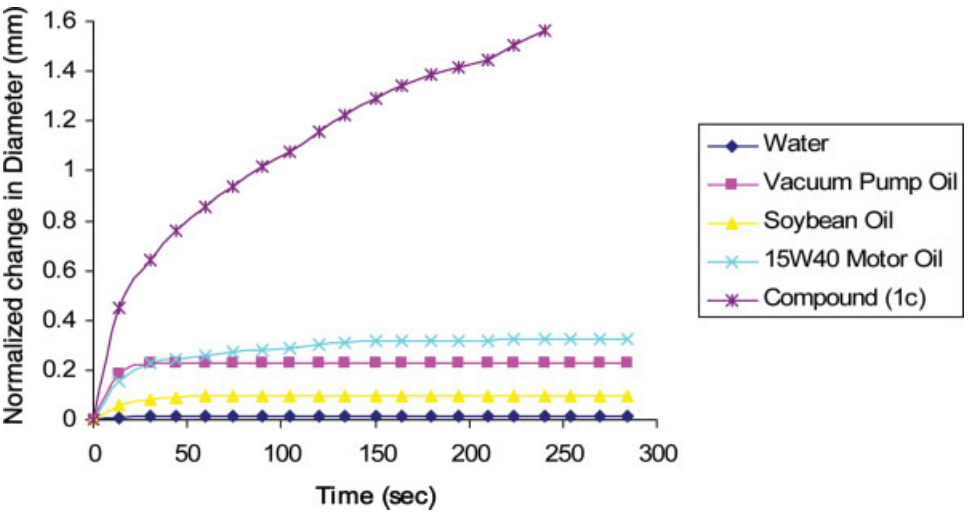


Figure 1 Pictorial representation of the movement of a variety of commercial oils and water. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

C, 45.54–43.57; H, 9.55–9.34; N, 2.21–1.88. Found: C, 44.48; H, 9.19; N, 2.49.

N-Ethyl-N,N-dihexyl-N-isobutyl ammonium bromide terminated polydimethyl siloxanes (7e)

FTIR: 3407, 2956, 2794, 2683, 2525, 1578, 1462, 1408, 1254, 1096, 1015 cm^{-1}. ^1H NMR ($CDCl_3$): 3.29–3.24 (m, 12H), 2.99–2.91 (m, 4H), 2.19–2.11 (m, 2H), 1.56 (t, 6H), 1.38–1.24 (m, 38H), 0.94 (t, 12H), 0.66–0.61 (m, 4H), 0.12–0.11 δ (m, 66H). A pale yellow solid was afforded in 58% yield. *Anal. Calcd. range*: C, 47.10–45.10; H, 9.76–9.53; N, 2.12–1.81. Found: C, 46.92; H, 9.41; N, 2.01.

N-Ethyl-N,N-dioctadecyl-N-isobutyl ammonium bromide terminated polydimethyl siloxanes (7f)

FTIR: 3407, 2948, 2848, 2798, 2740, 2675, 2513, 1963, 1578, 1474, 1404, 1370, 1258, 1100, 1015 cm^{-1}. ^1H NMR ($CDCl_3$): 3.25–3.17 (m, 12H), 2.94–2.87 (m, 4H), 1.99–1.94 (m, 2H), 1.53 (t, 6H), 1.32–1.21 (m, 126H), 0.89 (t, 12H), 0.66–0.62 (m, 4H), 0.17–0.01 δ (m, 66H). A pale yellow solid was afforded in 50% yield. *Anal. Calcd. range*: C, 60.19–57.40; H, 11.31–11.00; N, 1.40–1.26. Found: C, 57.94; H, 11.30; N, 1. 39.

Bacterial challenge preparation and antimicrobial testing protocol

General procedure for preparation of growth media

To a 1-L Erlenmeyer flask equipped with a stir bar was added 25.7 g Letheen broth™ (Difco Laboratories, Detroit, MI) and 1 L Milli-Q® filtered water. The mixture was stirred over low heat for 30 min. Aliquots (4.5 mL) of the resulting solution were added to autoclavable culture tubes (~ 200) to be used in subsequent serial dilutions. The test tubes were covered with plastic lids and autoclaved at 121°C (and 15 psi) for 25 min. Letheen broth was selected for its ability to neutralize the biocidal effect of quaternary ammonium salts so that continued antibacterial action would not occur after the serial dilution step.[19–22]

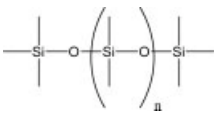
Preparation of bacteria

Staphylococcus aureus cells were grown in our laboratory according to standard microbiological techniques. *S. aureus* was harvested from an agar plate by removing a single CFU (colony forming unit), with a sterile inoculating loop, and placing it in Letheen broth. The culture was incubated at 28–30°C overnight in a shaking incubator. The cells were then pelleted by centrifugation at 3000 rpm and 18°C. The cells were then resuspended in 0.5% saline solution to achieve a density of about 10^7 CFU/mL as determined by McFarland turbidity standards.

Procedure for challenge tests

This method of evaluation is a well established serial dilution screening that has been employed by many research groups for decades.[23,24] A 1-μL aliquot of each water soluble ionic biocide was added to 1 mL of 10^7 CFU previously resuspended *S. aureus*. The resulting solution was vortexed and allowed to incubate at room temperature for 2 h. Afterwards, the resulting solution was serially diluted in Letheen broth and allowed to incubate at 35°C for 24 h. The tubes were read at the end of the 24-h incubation period. Positive growth was indicated by the presence of string-like filamentous growth of colonies of bacteria in solution, not mere murkiness, which may result form other

TABLE I
Tabulated Data of Methyl Terminated PDMS Examined



(1)

	M_W	Viscosity (cSt)[a]
1a	550	3.0
1b	950	7.0
1c	1250	10
1d	2000	20
1e	5970	100
1f	13,650	350
1g	28,000	1000
1h	49,350	5000
1i	116,500	60,000

[a] Viscosity specifications, ±10%.

forms of contamination. All data reported are an average of triplicates, and data is reported as log-reduction from a starting concentration of 10^7 CFU/mL.

Monitoring technique for movement of liquids

Movement of all liquids in this study was monitored optically with the use of an Intel-QX5 microscope at a magnification power of 10×. In all cases, photos were captured and stored electronically every 2 s for 5 min and, subsequently, every 5 min for 24 h. In most cases, 20 data points were taken from the first 5 min of data collection. Plotting additional data points resulted in a graph that was difficult to interpret because of overlapping data points that provided no additional useful information. It was noticed in most cases that the rate of change remained constant after the first 5 min, and therefore the remainder of the data points were not plotted to facilitate viewing the most useful data.

All liquid movement measurements were made on precleaned glass microscope slides in the horizontal position. A 1-μL aliquot of each liquid was placed on the center of the microscope slide using a calibrated micropipette. Because of the transparency of the microscope slide and the wide field of focus of the microscope at 10× power, a scale was placed under the glass slide. This resulted in the scale being recorded along with the movement of the various liquids. It was discovered that ambient dust frequently entered the spreading liquid and resulted in the liquid spreading in a noncircular pattern. Therefore, the use of a microscope slide as a protective cover along with spacers was necessary to prevent contamination from airborne dust particles present in the laboratory. The spacers prevented a sandwiching effect, while at the same time allowing air currents to affect the sample as they typically would in an open ambient environment. The use of an additional external light source was necessary to create a faint shadow to better visualize the advancing edge of the thinning liquid. It was discovered that the leading edge of the spreading liquid was best visualized with the naked eye; however, the need to make periodic measurements and accurately record the movement required the use of the low power microscope. All data was collected under ambient conditions to best simulate real world conditions.

After the liquids were allowed to spread, the video was examined and measurements were made for the average diameter of the advancing edges. The movement of all liquids reported is the average of three trials. All data was normalized to the initial liquid drop size at T_0. In those examples where the spread was not perfectly circular, multiple measurements of diameters were made and the average of those

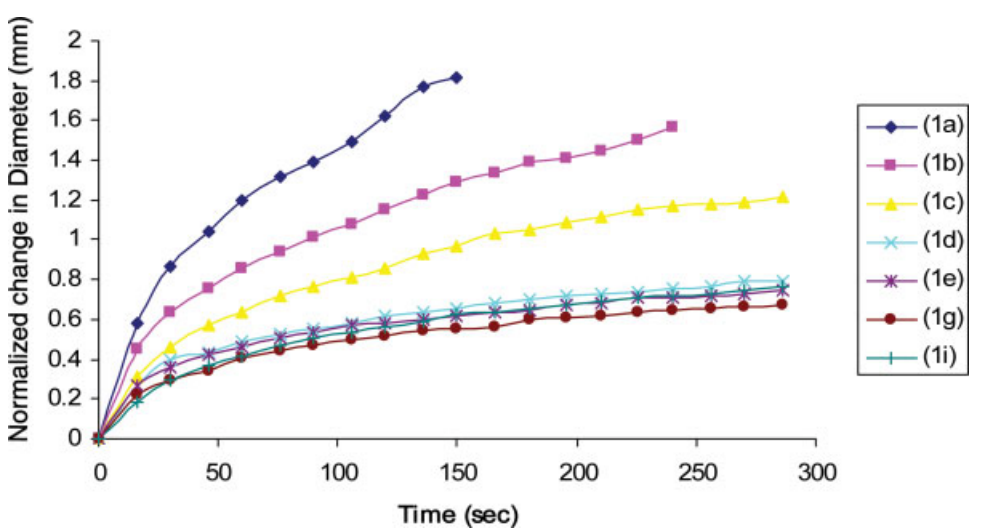


Figure 2 Comparison of the rate of movement of methyl-terminated PDMS by molecular weight/viscosity. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

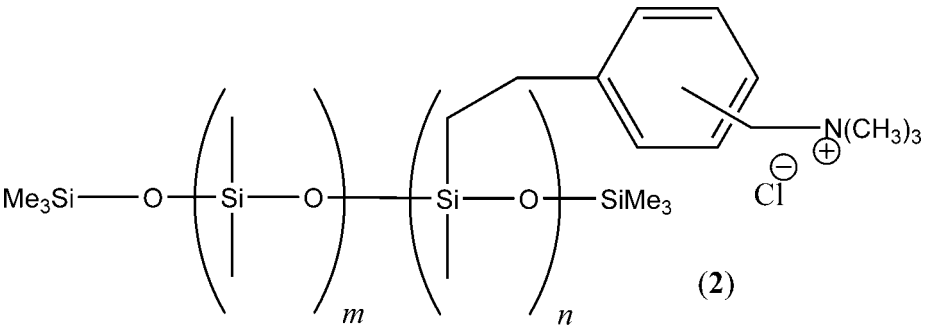


Figure 3 Structures of the block copolymer ionic PDMS (**2**).

obtained was used for plotting. The average change in diameter was plotted because of the errors encountered when attempting to use electronic software to calculate the area of the spreading liquid from the video. This was attributed to shadowing effects in the captured video.

All microscope slides and silicon wafers were cleaned prior to use for spreading studies. The manufacturer's pretreatment was removed by first soaking in chloroform and allowing the substrates to dry. The substrates were then soaked in an alcoholic potassium hydroxide solution for 2 h. After base treatment, the slides were washed with copious amounts of deionized water. Slides were dried in an oven and immediately used. Care was taken not to store cleaned substrates for prolonged periods of time to prevent contamination by ambient organics or dust particles.

RESULTS AND DISCUSSION

A variety of oils and lubricants were evaluated for their ability to wet a freshly cleaned glass substrate. As shown in Figure 1, the methyl-terminated PDMS (**1c**) possessed the highest rate of spread for those liquids evaluated. Soybean cooking oil, scientific vacuum pump oil, and commercial 15W40 motor oil all had very similar rates of spread. The rate of spread of these liquids was also compared to that of water on the same surface. As expected, water had the lowest rate of spread due to hydrogen bonding and high surface energy. From these results, it was believed that the addition of a surfactant to deionized water should affect its spreadability on the glass substrate. An aliquot of deionized water containing 0.001% (w/w) tetrabutylammonium bromide surfactant was examined. It was discovered that the rate of spread of the surfactant containing water wetted the surface more, initially; however, did not spread. Similarly, a solution containing 0.01% (w/w) surfactant was also examined with similar results. In both cases, the water containing surfactant spread more than water alone; however, neither spread as well as the other commercial oils examined. The plots of water with surfactant were omitted from Figure 1 for improved viewing.

As a result of examining a variety of commercial products, the self-spreading properties of the silicone oil (PDMS) far exceeded any other material examined. Consequently, it was concluded that the spread

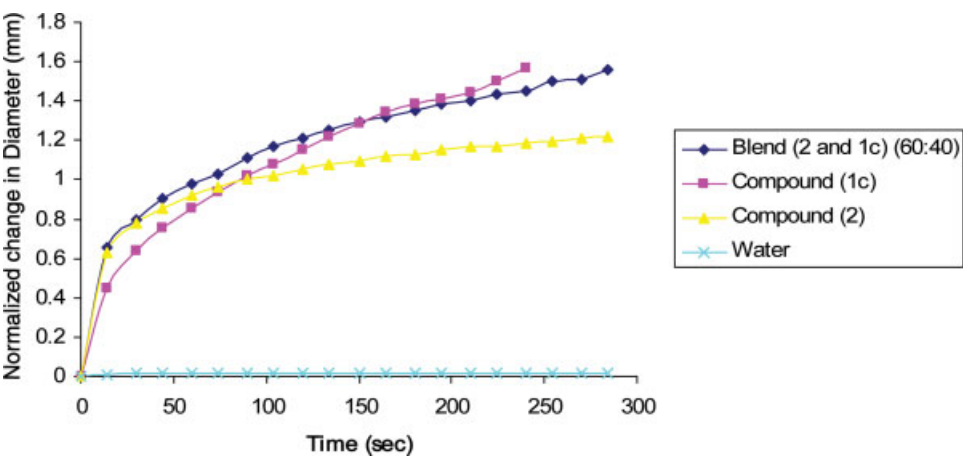


Figure 4 Comparison of the spread of PDMS (**1c**) with commercial ionic PDMS(2) and water. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

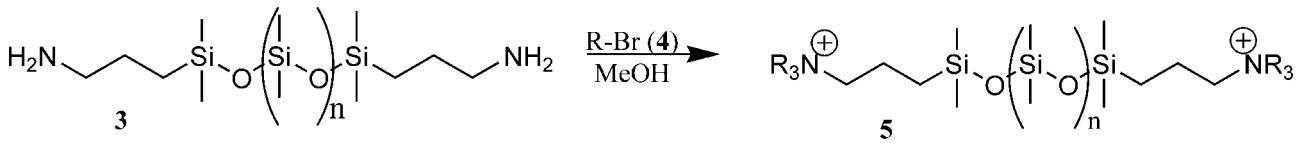


Figure 5 Synthetic scheme starting with primary amino silicone.

of the liquid was due to a combination of effects such as polarity, viscosity, surface energy, and the ability to conform to a variety of surfaces because of a flexible backbone, thus facilitating movement of the liquid across the substrate. As expected, molecules with a high degree of hydrogen bonding did not exhibit a high rate of spread. We, therefore, devoted the remainder of this study exclusively to the less polar molecules possessing a PDMS backbone.

As a result of data collected, we next examined a variety of commercially available methyl-terminated PDMS in a similar study to determine which molecular weight of compound **1** provided optimum mobility (Table I). As suspected, we observed an inverse correlation between the molecular weight of the PDMS oligomers and the rate of spread (Fig. 2). It was also concluded that the relative viscosities of the molecules examined played a major role in dictating the self-spreading properties. The low surface energy molecules deformed and moved as anticipated for all examples investigated (**1a-i**). Because of the similarity in movement of compounds **1d-i**, we elected to omit data for one compound (**1f**) from Figure 2 for optimal viewing clarity.

After examination of an array of methyl-terminated PDMS ranging in molecular weight from 550 to 116,500, our attention was turned to ionic silicones because of our belief that such oligomers could function as self-spreading antimicrobial liquids. It has been well documented by Bascom[25–27] that nonionic oils do spread on a variety of surfaces and are able to overcome the force of gravity; however, no study incorporated ionic liquids. The effect of an ionic moiety on a traditional molecule typically functions as an anchor, impairing mobility and subsequently reducing the rate of spread of the entire molecule. (Fig. 3)

In a comparative study of the spreadability of the commercially available ionic block copolymer PDMS (**2**) (M_W ~1800) with PDMS (**1c**) and water, the results were remarkably impressive (see Fig. 4). Much to our surprise and despite the numerous ionic centers within the molecule, (**2**) demonstrated good mobility. Compound **2** spread much better than water, yet was less mobile when compared to the unfunctionalized PDMS (**1c**) of similar molecular weight, as expected. Clearly, this demonstrates that the silicone backbone is able to overcome the ionic character present in the molecule which would be predicted to impair movement. It was concluded through this study that increased mobility could be achieved by blending nonionic compounds like **1c** with materials like compound **2**. We then resorted to examining a formulation of compounds **2** and **1c** in a 60:40 ratio (w/w). The blend performed remarkably well, in that it spread at a faster rate than the neat compound **2,** yet slower than the neat PDMS (**1c**). Surprisingly, no solubility incompatibility or phase separation was observed either in solution testing or on the glass surface. Despite the numerous quaternary ammonium moieties present, when compound **2** was evaluated for antimicrobial activity, it possessed very little biological activity against *Staphylococcus aureus*, frequently resulting in a reduction of only 1–2 log bacteria when subjected to solution testing consisting of 10^7 CFU/mL. These results were not sufficient for our disinfecting applications, and thus, we continued our efforts to increase antimicrobial activity while retaining spreading characteristics.

The findings from the spreading studies of (**2**) led us to conclude that the use of the PDMS low energy backbone coupled with fewer quaternary ammoniums would be advantageous. We believe that functionalization at the termini of the PDMS backbone may deter coiling of the molecules, potentially resulting in an increase in the antimicrobial activity of the compounds. Upon investigation of antimicrobial properties of other commercial ionic block PDMS, it was concluded that no commercial block ionic PDMS possessed the desired antimicrobial properties, thus the need for novel hybrid molecules was established.

TABLE II
Result of the Synthesis of (5) and Antimicrobial Evaluation

Compound no.	(**4**) R=	(**3**) M_W	*S. aureus*[a]
5a	$-C_2H_5$	900–1000	2
5b	$-nC_3H_7$	900–1000	2.6
5c	$-nC_4H_9$	900–1000	2.3
5d	$-nC_5H_{11}$	900–1000	4
5e	$-nC_6H_{13}$	900–1000	6
5f	$-nC_{18}H_{37}$	900–1000	7

[a] Log reduction results from solution testing; difference observed when 1 μL of 10^7 CFU/mL *S. aureus* was placed in 1 mL of water soluble ionic biocide.

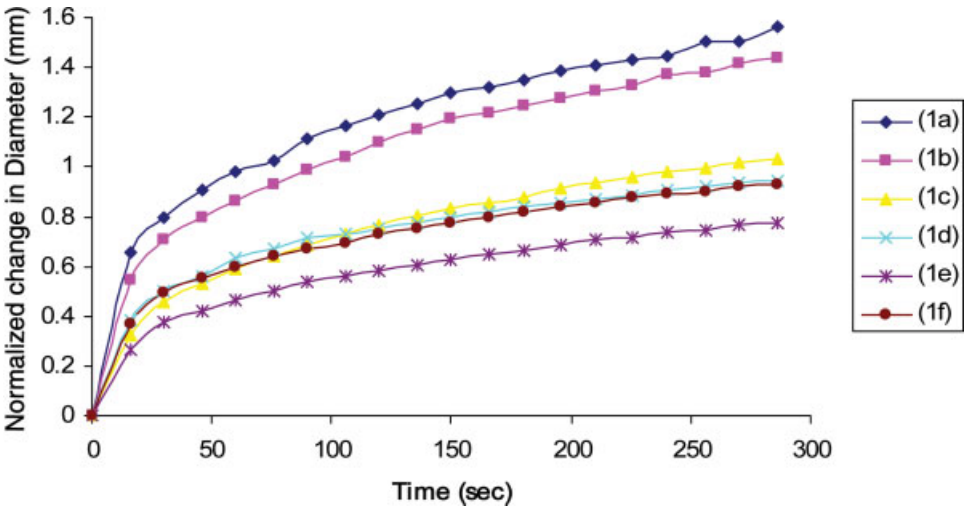


Figure 6 Comparison of the rate of spread of homologous series (**5**) blended with PDMS (**1c**). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In our attempt to increase antimicrobial activity while at the same time attempting to maintain the self-spreading properties of PDMS, we elected to incorporate only two ionic functionalities within the molecule, one at each terminus. We believed that this would lower the overall hydrogen bonding interactions of the molecule to the surface and in turn promote self-spreading of the molecule while also promoting antimicrobial activity. The synthetic scheme starting with the terminal primary amino PDMS molecule (**3**) by reaction with various alkyl halides (**4**) resulted in the formation of quaternary ammonium PDMS molecule (**5**) as seen in Figure 5. The homologous series of molecules were synthesized in good yield and because of their unique physical properties, they were easily purified. We found that by using an excess of alkyl halide (**4**), the reaction was forced to completion while facilitating removal of excess alkyl halide and solvent under reduced pressure. This procedure afforded a product of sufficient purity for use in this study. If desired, a purer product can be obtained via trituration with ethyl ether.

Using the biological protocol described earlier, each hybrid PDMS compound (**5a-f**) was evaluated in a solution test and the results are shown in Table II. A trend very similar to other traditional quaternary ammonium biocides was discovered. For the molecules examined, antimicrobial activity increased with the increased length of alkyl chain. Compounds **5d-f** clearly exhibited greater antimicrobial properties against the subjected Gram-positive bacteria. It was concluded that the direct attachment of the quaternary ammonium functionality to the PDMS backbone did not minimize the biological effect because of polarity or surface energy. Furthermore, it was concluded that the presence of three long alkyl groups directly attached to the quaternary nitrogen did not hinder antimicrobial activity because of steric effects, as has been observed in more widely used dimethyl ammonium series (frequently found in common household biocidal products). These results served as supporting evidence for our theory that possible coiling of the target molecules may result in reduced antimicrobial activity as observed for **2.** Contrast this with the increased antimicrobial activity of compounds **5a-f** which contains fewer ionic centers than **2**.

The movement of the homologous series **5** was analyzed; however, because many of the products were extremely viscous liquids or solids, their movement was minimal. We then resorted to taking advantage of the formulation blend that was successfully used with the polyquat (2) (see Fig. 4). Compound **5** was blended with **1c** in a 60:40 ratio (w/w) and then subjected to spread studies that are graphically depicted in Figure 6. Although compounds **5e** and **5f** afforded the greatest antimicrobial activity,

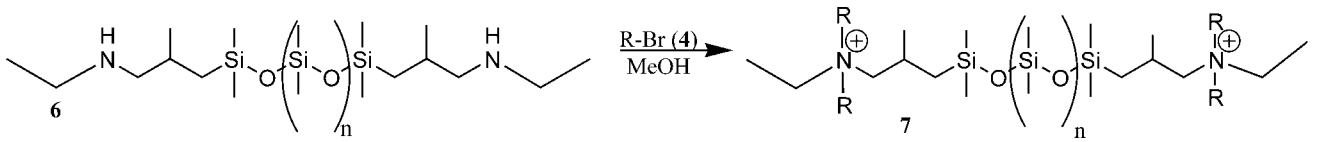


Figure 7 Synthetic scheme starting with secondary amino silicone.

TABLE III
Result of the Synthesis of (7) from Primary Diamino Polydimethylsiloxane (6)

Compound no.	(4) R=	(6) M_W	*S. aureus*[a]
7a	$-C_2H_5$	800–1000	2
7b	$-nC_3H_7$	800–1000	3
7c	$-nC_4H_9$	800–1000	3.6
7d	$-nC_5H_{11}$	800–1000	4.3
7e	$-nC_6H_{13}$	800–1000	6
7f	$-nC_{18}H_{37}$	800–1000	6

[a] Log reduction results from solution testing, difference observed when 1 μL of 10^7 CFU/mL *S. aureus* was placed in 1 mL of water soluble ionic biocide.

they were the least mobile. Compounds **5a** and **5b** resulted in the greatest rate of spread with the least biological activity; thus, supporting the idea that an inverse correlation exists between chain length and antimicrobial properties.

After examining the antimicrobial and self-spreading characteristics of each molecule in the homologous series of trialkyl ammonium PDMS (**5**), we next focused on increasing antimicrobial properties while simultaneously increasing mobility of the molecules, resulting in the formation of a self-spreading, self-decontaminating PDMS. Because of the antimicrobial effectiveness of unsymmetrical non-PDMS quaternary ammonium salts in other applications, we elected to synthesize and evaluate yet another homologous series of ionic PDMS molecules in an effort to increase mobility and antimicrobial activity. Starting with a secondary amino PDMS species (**6**), as depicted in Figure 7, and similar to that depicted earlier, the diamino PDMS molecule was reacted with a variety of alkyl halides (**4**) resulting in the second homologous series of hybrid quaternary ammonium PDMS oligomers (**7**).

As with compounds **5a-f**, the syntheses of compounds **7a-f** were accomplished in good yields and all were easily isolated. Each oligomer was subjected to solution antimicrobial evaluation and afforded good results. As seen in the data for compounds **5a-f**, there was a direct correlation with antimicrobial properties and alkyl chain length. Although very similar, the antimicrobial properties of compound **5f** appear to be marginally greater than those exhibited by any of the compounds **7a-f** (Table III).

After observing similar to slightly reduced antimicrobial properties for **7** (when compared to **5**), a similar study of spread was performed. The physical properties of **7** were very similar to those described earlier for compounds **5a-f**. Therefore, spread measurements were performed as a blend with **1c** in a 60:40 ratio (w/w) as described previously and are depicted in Figure 8. Very similar results were seen for this homologous series as well. Although compounds **7e** and **7f** afforded the greatest antimicrobial activity, they resulted in very little spread. Compounds **7a** and **7b** resulted in the greatest rate of spread with least antimicrobial activity. These results are in agreement with the test data for compounds **5a-f**.

Although all previously mentioned studies were conducted on glass, we also examined the ability of a blend of compound **5b** and **1c** (60:40) (w/w) to self-spread on a previously cleaned silicon wafer. A 1-μL sample of the blend was placed in the center of a 2-in. diameter silicon wafer. Interference patterns began to form after a few hours and continued to develop with time. As seen in Figure 9, interference patterns developed after allowing the mixture to

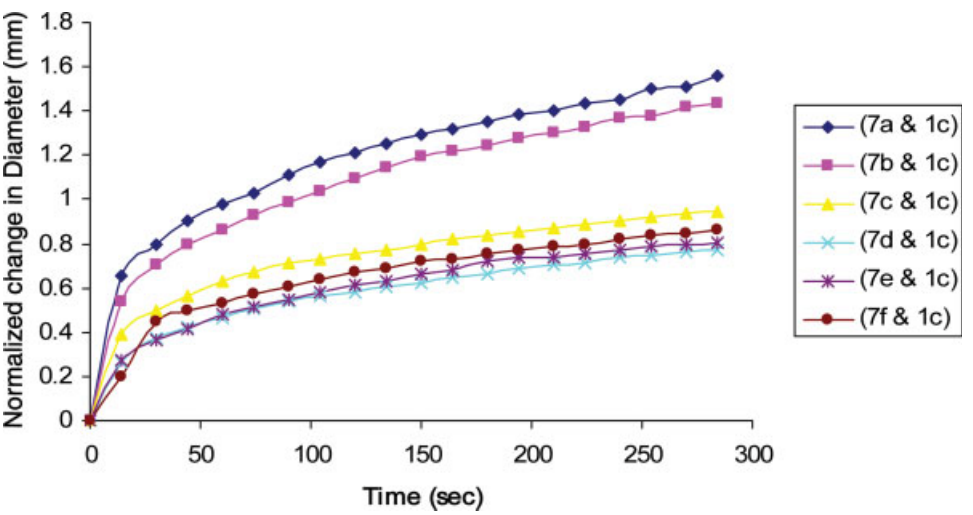


Figure 8 Rate of spread of homologous series (**7**) blended with PDMS (**1c**) (60 : 40 ratio). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

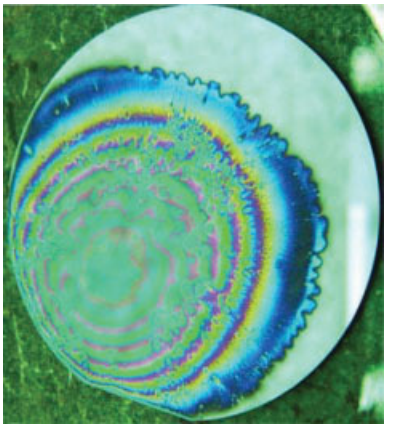


Figure 9 Photo of **5f** and **1c** blend spreading on a polished silica wafer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

spread for 24 h. The presence of interference fringe patterns in thin liquid films indicates film thickness is on the same order of magnitude as the wavelength of light. Maximum intensities in the pattern are observed when the film thickness is a multiple of [1/4] of the wavelength of the reflected light. With additional time, the liquid continued to spread on the wafer and the observed rainbow interference pattern became a uniform violet color indicating that the thickness of the liquid on the wafer was uniformly approaching [1/4] the wavelength of light. After allowing the coated wafer to sit for an extended period of time, the liquid eventually spread off of the edge of the wafer and coated the bottom of the wafer and began to coat the Petri dish in which the wafer had been placed to protect it from ambient dust. Since the film thickness varied from thicker to thinner in a uniform manner, as the film spread a series of ''rainbows'' appear; a new one every time the film thickness decreased by a multiple of [1/4] of the wavelength of the given ''color.'' Figure 10 illustrates the relative spreading profile of the liquid along the path indicated with an arrow in Figure 9. The graph correlates harmonic number (n), also referred to frequently as multiples of wavelength of any specified color band, to distance across the wafer. Preliminary approximations were made given the amount of liquid applied and the surface area of the wafer. If the liquid were allowed to spread to form a uniform coating, it is anticipated that the thickness of the liquid should approach 500 nm. As can be seen from the profile of the advancing edge using this crude methodology, it is very consistent with that of previous reports by Bascom.[26]

Although the mechanism of spread in our study has not received much attention, more extensive surface material spread studies are underway along with a more complete antimicrobial screening against a greater array of both Gram-positive and Gram-negative bacteria. Further optimization of biocidal functional group and an examination of potential synergistic effects of subsequent ionic blends remain under investigation. It is envisioned that the synthesis of and optimized compound that would facilitate spread while maximizing antimicrobial activity is an achievable goal.

CONCLUSIONS

In conclusion, we report the synthesis and characterization of two homologous series of PDMS compounds that can be used as self-spreading biocides. The spreading properties of the synthesized compounds are reported and compared to a wide variety of common oils and liquids. The spreading properties of the PDMS compounds are superior to many of the common oils and liquids tested in this study, thus making them good candidates for use as self-spreading biocides on surfaces that are difficult to access. A preliminary study of the antimicrobial properties of the newly synthesized molecules is reported and the information will be used to guide future studies. Although we have demonstrated progress toward the synthesis of self-spreading antimicrobial oils, many properties need to be improved. It is believed that the functional groups employed in **5f** can be incorporated into oligomers such that they will exhibit improved spreading characteristics while

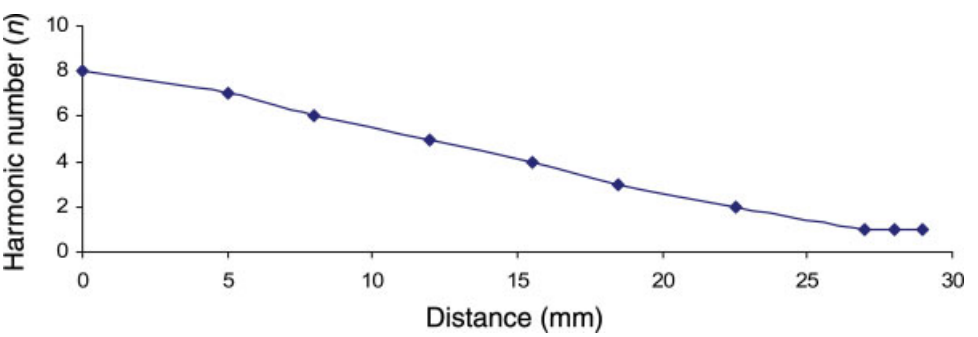


Figure 10 Thickness profile of the spreading liquid based on interference fringes observed in Figure 9.

retaining the desired antimicrobial activity. Future work will be directed toward that goal.

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