Biocidal Polymers Active by Contact. V. Synthesis of Polysiloxanes with Biocidal Activity

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ABSTRACT: Polysiloxanes with 3-(alkyldimethylammonio)propyl pendant groups were synthesized by quaternization of *n*-octyldimethylamine or *n*-dodecyldimethylamine with linear polysiloxanes containing 3-chloropropyl groups and/or 3-bromopropyl groups attached to silicon atoms. The precursor polysiloxanes, poly[(3-chloropropyl)-methylsiloxane] homopolymer and various copolymers containing (3-halogenopropyl)-methylsiloxane and dimethylsiloxane units, were obtained by equilibrium cationic polymerization of linear and cyclic siloxanes with (3-halogenopropyl)methylsiloxane units. The polysiloxanes bearing quaternary ammonium salts (QAS) showed bactericidal activity against bacteria such as *Escherichia coli* and *Aeromonas hydrophila* when incorporated in a polysiloxane network. The activity was retained after 66 days of immersion in water. The QAS-containing polysiloxanes are also active in aqueous solution. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1005–1012, 2000

Key words: functional polysiloxanes; quaternary ammonium salts; macromolecular biocide; antibacterial activity

INTRODUCTION

The invasion of polymers by bacteria, fungi, and other micro-organisms is manifested by loss of mechanical properties, surface degradation, discoloration, staining, and other polymer deteriorations leading to loss of its appearance and properties. Addition of a biocide during compounding is the most usual way to prevent the colonization of polymers by micro-organisms. However, the biocide released from polymer may be a hazard to the environment, and protection is limited in time. Fixation of the biocide on the polymer backbone by an hydrolyzable bond results only in a better control of the time during which the polymer is protected, but does not solve the problem of toxicity.[1–3]

Quaternary ammonium salts (QAS) with one long alkyl chain substituent having at least eight carbon atoms have been known for a long time as active biocides in water.[4,5] It is known that QAS exert their biocidal activity by interaction with the cell wall of bacteria.[6–8] In the search of non-leaching "environmentally friendly" biocides, the recent concept of QAS biocides fixed to a polymer in a permanent way by a stable chemical bond has been developed.[9–16] Soluble QAS-bearing polymers were found to be more active biocides than the corresponding monomers,[10–12] which may be explained by the larger density of charge on the polymer making their interaction with the cellu-

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lar wall more efficient. In the case of insoluble crosslinked polymers, reported results are at variance. Crosslinked polyvinylpyridinium halide claimed to capture bacterial cells by electrostatic interaction, but let them live.[16] Dow Corning researchers have developed a reactive silane $(MeO)_3Si(CH_2)_3N^+Me_2C_{18}H_{37}Cl^-$ (DC 5700) able to react with many surfaces such as glass, cotton, or polyester fibers[17] or polyurethane foams.[18] The treated materials show algicidal and bactericidal properties that are maintained after repeated washings, and no apparent leaching is observed. However, Clarkson and Evans[19] prepared a vulcanized silicone elastomer by reacting the above DC 5700 silane with a hydroxy-ended polydimethylsiloxane. They found that QAS was not totally bound to the polymer, and that the biocidal activity against a marine fouling diatom was due exclusively to the free QAS leaching out of the silicone. After complete Soxhlet extraction, the polymer retained no biocidal activity.

On the other hand, QAS-substituted hydroxytelechelic polybutadiene have been prepared and incorporated in a polyurethane network.[14] The same was done with a polysiloxane bearing both QAS and alcohol functions.[20] In both cases, a very high biocidal activity and a fairly good permanency in water were observed, and interpreted as an intrinsic surface property of the polymer films being able to kill bacteria by a direct contact between the solid film and the bacteria cells.

Although it is very difficult to rule out definitely the possibility that some leachable compounds take a small part in the observed biocidal activity, all results show that polymers containing permanently bound QAS give advantage over materials functioning by controlled release of a low molecular weight biocide, as they show much better durability without or with very low liberation of toxic products in the environment. Recently, Daudet has shown that an interpenetrated network (IPN) consisting of a linear QAS-substituted polysiloxane of high molecular weight dispersed in a polydimethylsiloxane network had fungicidal properties both by direct contact and by diffusion, and a much better durability than conventional fungicidal silicone mastics used for sanitary applications.[21]

The purpose of this work is to explore a new route for the synthesis of biocidal QAS-containing polysiloxane involving the direct quaternization of a 3-halogenopropyl-substituted polysiloxane used as a precursor. This route seems to be better than the route consisting of the hydrosilylation of a polysiloxane copolymer containing methylhydrogensiloxane units,[20] as it permits one to avoid using allyldimethylamine, which is expensive and toxic. On the other hand, 3-chloropropyl-substituted polysiloxanes are easily obtained by hydrolytic polycondensation of $[Cl(CH_2)_3]MeSiCl_2$, which is an industrial product,[22] followed by equilibration of the hydrolysate or its coequilibration with octamethylcyclotetrasiloxane, D_4, a common monomer in the silicone industry. This route was used to synthesize homopolymers and statistical copolymers of controlled compositions and QAS-containing polymers with Cl^- and Br^- counterions were also prepared.

The second aim of this work was to verify that the QAS-containing polysiloxanes obtained by this simpler and cheaper route do not differ in biocidal activity from those obtained by the amine-substituted polysiloxane route.

EXPERIMENTAL

Synthesis of Poly(3-chloropropyl)methylsiloxane, 3

Water, 18 g (1.0 mol), was slowly introduced to stirred solution of 95.8 g (0.5 mol) of (3-chloropropyl)methyldichlorosilane (ABCR) in 200 mL of diethyl ether. Then the reaction mixture was stirred in room temperature for about 4 h and kept 1 day over $CaCl_2$. After filtration, the solvent was removed and the hydrolysate **2** was heated in 80°C/10^{-3} mmHg for 4 h. The mixture of 65.5 g (0.6 mol of siloxane unit) of the hydrolysate and 0.97 g (0.006 mol) of hexamethyldisiloxane was kept in room temperature for 24 h with 0.01 mL ($1 \cdot 10^{-3}$ mol) of trifluoromethanesulfonic acid. Then, the polymer formed was washed three times with water and precipitated from its methylene chloride solution in methanol. The precipitation procedure was repeated four times. After drying 24 h over $CaCl_2$, the polymer was heated 6 h in 80°C/10^{-3} mmHg. Thirty-two grams, yield 50%, of polymer **3** was obtained. The polymer was characterized by SEC (Table I) and by ^{1}H-, ^{13}C-, and ^{29}Si-NMR.

Synthesis of Poly[(3-chloropropyl)methylsiloxane-*co*-dimethylsiloxane, 4

The mixture of (3-chloromethyl)methyldichlorosilane hydrolysate **2**, 20 g (0.154 mol siloxane unit), octamethylcyclotetrasiloxane, 34.2 g (0.462 mol siloxane unit), hexamethyldisiloxane 0.49 g

Table I Structures of the Halogenated Polysiloxanes

Ref.	% Halogenated Units (NMR)	M_n (g · mol^{-1}) SEC (PS Equiv.)	M_w/M_n
3	100 (Cl)	10000	1.94
4	21 (Cl)	26620	1.55
5	67 (Br)	4100	1.6
8	54 (Cl) 46 (Br)	5100	1.47
11	17.5 (Br)	10500	1.53

(0.003 mol), and 0.1 ml (10^{-3} mol) of CF_3SO_3H was kept in room temperature for 24 h. The purification of polymer **4** was performed according to the same procedure as was used in the purification of polymer **3**. Twenty-six grams, yield 50% of copolymer **4** was obtained, and characterized by SEC (Table I) and by ^{1}H-, ^{13}C-, and ^{29}Si-NMR.

Synthesis of Poly[(3-bromopropyl)methylsiloxane-*co*-dimethylsiloxane], 5

Allyl bromide 60 g (0.5 mol) and hexachloroplatinic acid in cyclohexanone ($3 \cdot 10^{-5}$ mol of H_2PtCl_6) was placed in a 250-mL flask under atmosphere of prepurified argon. The flask was thermostated in 60°C, and after 15 min methyldichlorosilane, 86 g (0.75 mol) was slowly added. The reaction was carried out for 72 h at 60°C. Distillation gave 79 g (0.3 mol) (3-bromopropyl)-methyldichlorosilane, **6**, b.p. 40–50°C/2 mmHg, yield 60%. Purity of **6** was checked by gas chromatography, and was 95%. Hydrolysate of (3-bromopropyl) methyldichlorosilane, **7**, was obtained from **6**, and copolymer **5** was prepared from hydrolysate **7**, octamethylcyclotetrasiloxane and hexamethyldisiloxane in an analogous way to that described in the preparation of copolymer **4**. Similarly, poly[(3-bromopropyl)methylsiloxane-*co*-(3-chloropropyl)methylsiloxane], **8**, was synthesized from hydrolysates **2** and **7**, and hexamethyldisiloxane (yield 50%). Copolymers **5** and **8** were characterized by ^{1}H-NMR and SEC (Table I).

Studies of Quaternization of 3-Halogenopropyl-Substituted Polysiloxanes

Poly[(3-chloropropyl)methylsiloxane-*co*-dimethylsiloxane], **4**, 0.52 g ($1.44 \cdot 10^{-3}$ mol) together with 0.28 g ($1.75 \cdot 10^{-3}$ mol) of *n*-octyldimethylamine (20% excess) in 10 mL of propanol was heated at 97°C on a thermostating bath in a flask fitted with stirrer, reflux condenser, and a stopcock through which samples were withdrawn. The extent of reaction was followed by ^{1}H-NMR. Solvent was removed from the sample by distillation before the analysis. The spectrum of the partially quaternized copolymer **4** is similar to that shown for the partially quaternized homopolymer shown in Figure 3. The difference is only in the intensity of the signal of CH_3—Si at about 0 ppm. The conversion was calculated on the basis of h_1—the integration of the signal of CH_3—Si—and of h_2—the total integration of signals of protons d_1, d′, e′, and f′, as marked on Figure 3, which appear in the range 3.0 to 3.8 ppm. The conversion X was calculated from eq. (1).

$$X = \frac{1}{8}\left[\frac{6 - 3y}{y}\frac{h_2}{h_1} - 2\right] \quad (1)$$

where y is the fraction of siloxane units bearing 3-chloropropyl function in the copolymer. Studies of quaternization of other copolymers and studies of the reaction under various conditions were made in a similar way.

Studies of Bactericidal Properties

Test by Contact

Copolymer **4** (119 g) fully quaternized with dimethyldodecylamine (Q17 in Table III) was added to 170 g of a mastic made of a mixture of polydimethylsiloxanes and a curing system. The mastic was spred in thin films (100 μm thickness) on a plate of glass or molded in the shape of small disks (thickness 5 mm, diameter 27 mm). The samples were immersed into a suspension of bacteria at room temperature and left in contact for 2 h. The initial number of bacteria and the number of survivors after the contact with the mastic were counted as previously described.[14] Data for three species of bacteria are presented in Table IV.

Test of Aging

The film of the mastic was immersed for 66 days in water and continuously stirred by a mechanical stirrer. Results are presented in Table V.

Test in Solution

A solution containing the quaternized polysiloxane Q17 at a concentration of $5.3 \cdot 10^{-4}$ mol · l^{-1}

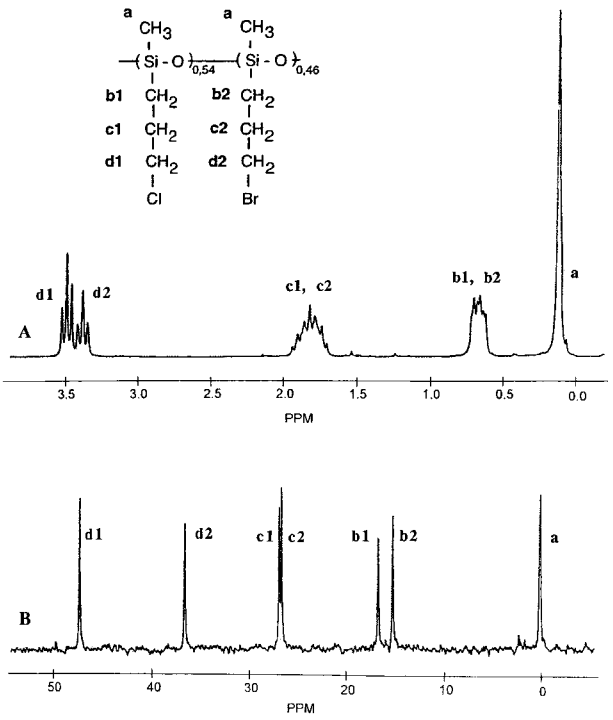


Figure 1 NMR spectra of poly[(3-bromopropyl)-methylsiloxane-*co*-poly(3-chloropropyl) methylsiloxane] **8**. (A) ^{1}H-NMR spectrum; (B) ^{13}C-NMR spectrum.

was inoculated with a known number of *Escherichia coli*. After to 2 h, the survivors were counted using the usual procedure.

RESULTS AND DISCUSSION

Synthesis of Halogenoalkyl Polysiloxanes

The homopolymer of (3-chloropropyl)methylsiloxane, **3**, was obtained in a two-step synthesis starting from (3-chloropropyl)methyldichlorosilane, **1**. First, compound **1** was submitted to hydrolytic polycondensation in a diethylether–water two-phase system. Hydrolysate **2**, containing cyclic siloxane oligomers, mostly tetramer 1,3,5,7-tetra(3-chloropropyl)-1,3,5,7-tetramethylcyclotetrasiloxane, was obtained. Then, it was equilibrated in bulk with hexamethyldisiloxane (MM) in the presence of CF_3SO_3H to obtain polymer **3** of the number-average molecular weight $\overline{M}_n = 10^4$ g · mol^{-1}, which was separated from cyclics by precipitation from methylene dichloride solution in methanol and characterized by Size-Exclusion Chromatography (SEC) and ^{1}H-NMR (Table I). Poly[(3-chloropropyl) methylsiloxane-*co*-dimethylsiloxane], **4**, was obtained in a similar way by coequilibration of **2** with octamethylcyclotetrasiloxane (D_4) and MM.

Copolymers of (3-bromopropyl)methylsiloxane with dimethylsiloxane (**5**, **11**) and with (3-chloropropyl)methylsiloxane (**8**) were synthesized in an analogous way. (3-Bromopropyl)methyldichlorosilane (**6**) was hydrolyzed, and the resulting hydrolysate (**7**), containing mostly the cyclic tetramer 1,3,5,7-tetra(3-bromopropyl)-1,3,5,7-tetramethyl cyclosiloxane, was copolymerized either with D_4 or with the hydrolysate **2** in the presence of MM and CF_3SO_3H. The characteristics of all these copolymers are presented in Table I.

The composition of the copolymers was determined by ^{1}H-NMR spectroscopy. As shown in Figure 1(A), this was also possible in the case of copolymer **8**, containing chlorine-substituted units and bromine-substituted units because the signals of CH_2Cl and CH_2Br are distinct. ^{13}C-NMR spectra confirmed the structures [Fig. 1(B)].

^{29}Si-NMR spectrum of copolymer **4** is presented in Figure 2. It was used to determine the distribution of the functional siloxane units by a sequential analysis made on the triad level. The experimental values are compared in Table II with those calculated for a random placement. The distribution was close to statistical.

Quaternization

Quaternization of the 3-halogenopropyl–substituted polymer and copolymers presented in Table

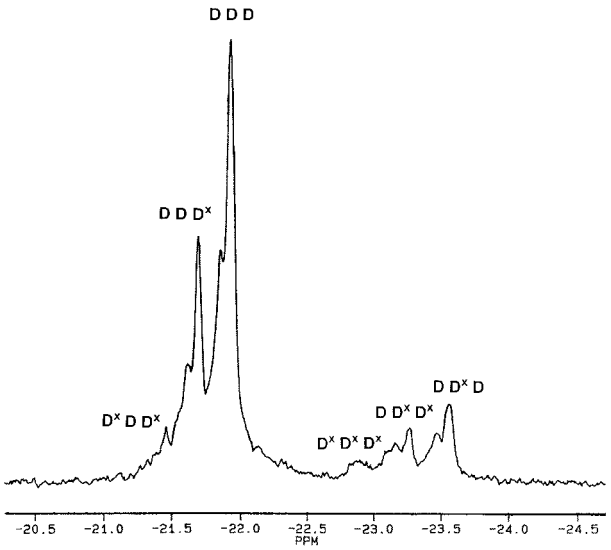


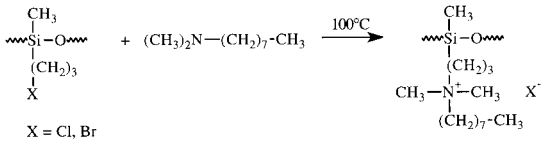
Figure 2 ^{29}Si-NMR spectrum of poly[(3-chloropropyl)methylsiloxane-*co*-dimethylsiloxane] **4** for the analysis of triads.

Table II Sequential Analysis of Poly[(3-chloropropyl)methylsiloxane-co-dimethylsiloxane], 4

Triad	^{29}Si NMR δ (ppm/TMS)	Contribution %	
		Experimental	Calculated[a]
DD^XD	−23.5	10.3	13.5
DD^XD^X	−23.3	8.4	7.7
$D^XD^XD^X$	−22.9	3.6	1.1
DDD	−21.9	47.6	46.9
DDD^X	−21.7	23.5	26.9
D^XDD^X	−21.5	6.6	3.9

[a] Assuming random placement of units D and D^X.

I with *n*-octyldimethyl amine was performed in bulk and in solution according to eq. (2).



(2)

The extent of the reaction was followed by ^{1}H-NMR analysis of samples withdrawn from the reaction mixture. Typical ^{1}H-NMR spectrum of the polysiloxane partially quaternized is presented in Figure 3.

Quaternization of homopolymer **3** in bulk at 98°C performed under conditions used in ref. 23 proceeded very slowly despite the very large excess of the amine used to lower the viscosity of the medium (Experiment Q20 in Table III). Using 2.65 times the stoichiometric amount of amine, the conversion of the chlorine groups was about 50% after 4 h.

The reaction proceeds faster in some polar protic solvents, which is characteristic for the Menschutkin reaction leading to the generation of charge. To make comparisons easier, the rates were compared as second-order rate constants calculated from the initial rate, R_o, according to eq. (3):

$$k = \frac{R_0}{[X]_0[NR_3]_0} \tag{3}$$

Comparison of the reaction rates in different solvents is shown in Table III. The best choice appears to be boiling propanol in which the reaction was completed in about 46 h using a 20% excess of amine and a concentration of chlorine groups equal to 0.37 mol · L^{-1}. Comparison of Experi-

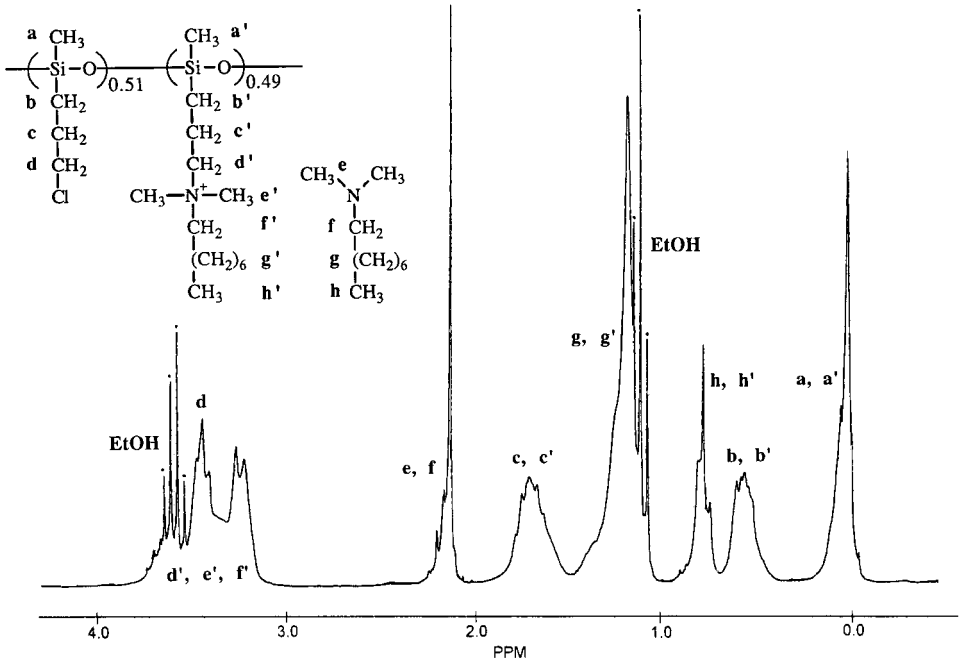


Figure 3 ^{1}H-NMR spectrum of the sample withdrawn from the reaction mixture after 48 h 30 min during the quaternization of poly[(3-chloropropyl)methylsiloxane] **3** with dimethyloctylamine in ethanol in 79°C (Experiment Q1, yield: 49%).

Table III Second-Order Rate Constants for Quaternization of Halogenated Polysiloxanes with Dimethyloctylamine in Various Conditions

Exp. No.	Halogenated Polysiloxane	$[X]_0$ (mol · L^{-1})	$[NR_3]_0$ (mol · L^{-1})	T (°C)	Solvent	k (L · mol^{-1} · h^{-1})
Q20	**3**	1.83	4.865	98	None	$\cdot 2.3 \cdot 10^{-2}$
Q1	**3**	0.366	0.440	79	Ethanol	$2.4 \cdot 10^{-2}$
Q2	**3**	0.366	0.438	97	Propanol	$5.2 \cdot 10^{-2}$
Q3	**3**	0.366	0.365	97	Propanol	$5.7 \cdot 10^{-2}$
Q6	**3**	0.320	0.304	101	Dioxane	$3.6 \cdot 10^{-2}$
Q7	**3**	0.192	0.195	100	Acetone–Dioxane (1 : 1)	$3.8 \cdot 10^{-2}$
Q8	**3**	0.415	0.405	56	Acetone	$2.6 \cdot 10^{-3}$
Q13	**5**	0.195	0.233	97	Propanol	2.1
Q15	**8**	[Br] = 0.133 [Cl] = 0.156	0.347	97	Propanol–Dioxane (10 : 1)	1.00
Q16	**4**	0.132	0.181	97	Propanol–Dioxane (10 : 1)	$5.0 \cdot 10^{-2}$
Q17[a]	**4**	0.466	0.639	97	Propanol	$2.0 \cdot 10^{-2}$
Q21	**11**	0.132	0.181	97	Propanol	2.7

[a] Quaternization with dimethyldodecylamine.

ments Q2 and Q3 (homopolymer with different concentration of amine) with Q16 (copolysiloxane with 21% chlorinated groups) show that eq. (3) holds remarkably. However, the reaction does not obey an internal second-order law, because the reaction rate remains almost constant when the reaction proceeds, which corresponds to an apparent zero order (see Figs. 4 and 5). This effect may be explained by a change of conformation of the polymer chain due to the formation of ions that may significantly accelerate the reaction as the yield increases. As expected, the quaternization is much faster with bromine-substituted polysiloxane than with its chlorine analogue (see Fig. 5). From the initial rate constants for reactions of copolymers **4** and **11** (Experiments Q16 and Q21 in Table III) in boiling propanol, the ratio of the apparent second-order rate constants k_{Br}/k_{Cl} is about 50.

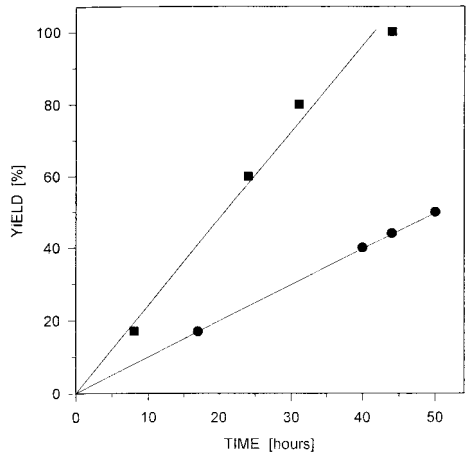


Figure 4 Comparison of the rates of quaternization in different solvents and at different temperatures. ● ethanol at 79°C (Experiment Q1); ■ propanol at 97°C (Experiment Q2).

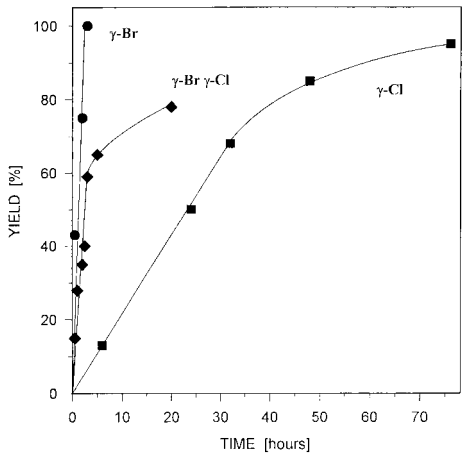


Figure 5 Influence of the nature of halogen on the rate of quaternization in propanol at 97°C. ● Poly[(3-bromopropyl)methylsiloxane-*co*-dimethylsiloxane] **11** (Experiment Q21); ■ poly[(3-chloropropyl) methylsiloxane-*co*-dimethylsiloxane] **4** (Experiment Q16); ◆ poly[(3-bromopropyl)methylsiloxane-*co*-(3-chloropropyl)methylsiloxane] **8** (Exp. Q15).

Table IV Bactericidal Activity of a Silicone Mastic Containing the QAS-Containing Polysiloxane Q17. Time of Contact: 2 h at 20°C

Strain	N_0	N	log (N_0/N)
Escherichia coli	$1.24 \cdot 10^6$	$2.7 \cdot 10^4$	1.67
Aeromonas h.	$3.65 \cdot 10^6$	$1 \cdot 10^6$	0.55
Pseudomonas a.	$8 \cdot 10^7$	$>1 \cdot 10^7$	<0.9

The course of the quaternization of the copolymer **8** having 46% of siloxane units substituted with bromine and the remaining units substituted with chlorine is shown in Figure 5. The reaction proceeds in two steps. A fast reaction of the bromine groups is followed by a very slow conversion of the chlorine groups. The initial apparent second-order rate constant in this experiment ($k = 1.0\ \mathrm{L \cdot mol^{-1} \cdot h^{-1}}$) is in good agreement with the weighted average of the respective rate constants for bromine and chlorine:

$$k_{\mathrm{app}} = 0.46k_{Br} + 0.54k_{\mathrm{Cl}} \approx 1.181 \cdot \mathrm{mol^{-1} \cdot h^{-1}} \quad (4)$$

Experiment Q17, with *N,N*-dimethyldodecylamine, was slower than experiments carried out with *N,N*-dimethyloctylamine in the same conditions by a factor of two to three.

Bactericidal Properties

Copolymer Q17 containing 21% of $N(CH_3)_2C_{12}H_{25}^+ Cl^-$ groups was selected for the study of the bactericidal properties (Table III). It was used as additive in a mastic made of a vulcanized silicone elastomer.[21] The QAS-containing polysiloxane was added during compounding at 6.5% weight to obtain a bulk concentration of $1 \cdot 10^{-4}$ mol QAS per gram of mastic.

Two tests of bactericidal properties were performed with this mastic: a test by diffusion, and a test by contact. The test by diffusion showed that the amount of active product released from the mastic (if any) was too low to produce an inhibition zone around the sample. The results of the test by contact are summarized in Table IV. The bactericidal activity is measured by the logarithmic reduction ratio, $\log(N_o/N)$, where N_o is the initial number of bacteria, and N, the number of survivors after 2 h of contact with the mastic.

The test was made for three types of Gram-negative bacteria: *Escherichia coli* (ATCC 10536, CNCM 54127), *Aeromonas hydrophila* (ATCC 7965), and *Pseudomonas aeruginosa* (ATCC 27853, CIP 76110). The last species is known to be resistant to antibiotics. Results presented in Table IV indicate that the QAS-substituted polysiloxanes show a high bactericidal activity by contact towards *Escherichia coli* and a lower activity towards *Aeromonas hydrophila* and *Pseudomonas aeruginosa.*

The biocidal activity of the samples was also measured after immersion in water with moderate stirring for a period of 66 days. Results of the test carried out for *Escherichia coli* are presented in Table V.

They indicate that the mastic preserves its biocidal activity, which is even larger than before immersion in the case of a thick sample (5 mm). This observation is probably connected with the hydrophilic surrounding of the mastic film during the aging experiment, which causes the migration of the water-soluble QAS polysiloxanes to the film surface. Thus, the availability of the active QAS for contact with bacteria is better. Effectively, the high molecular weight QAS-containing polysiloxane Q17 dispersed into the network of a polysiloxane mastic constitutes a semi-interpenetrated network (IPN). Due to entanglements, its migration towards the surface and its release in the surrounding medium should be very slow. Semi-IPN have been shown to realize an excellent compromise between low molecular weight biocides used as additives and QAS-containing polymers covalently attached to the surface.[21] It is worth noting that the biocidal activity of the present semi-IPN after 66 days of immersion in water is comparable to that of PU-films cured with a QAS-modified polysiloxane ($\log N_o/N = 3.7$ after 30 days in water[20]) or with a QAS-modified polybutadiene [$\log(N_o/N) = 3.2$ after 78 days in water[15]].

Table V Effect of Aging in Water of a Silicone Mastic Containing the QAS-Containing Polysiloxane Q17. Strain: *Escherichia coli.* Time of contact: 2 h at 20°C

Sample	N_0	N	log (N_0/N)
Thin Film Aged 66 Days	$1.1 \cdot 10^6$	$1.9 \cdot 10^4$	1.76
Thick Sample Aged 66 Days	$1.64 \cdot 10^6$	$1 \cdot 10^3$	3.22

As the QAS-substituted polysiloxane Q17 containing 21% hydrophilic QAS was soluble in water, its bactericidal activity could be also studied in water solution. One milligram of the copolymer was dissolved in 3 mL of water to give a QAS concentration equal to $5.3 \cdot 10^{-4}$ mol $\cdot$ l^{-1}. A number of $4.8 \cdot 10^7$ *Escherichia coli* was added. After 2 h, the number of survivors was 130, which corresponds to a logarithmic reduction ratio $\log(N_o/N) = 5.6$. Thus, the QAS-substituted siloxane copolymer is also a powerful bactericide in water solution.

CONCLUSIONS

Polysiloxanes containing (3-halogenopropyl)-methylsiloxane units are easy to prepare and are suitable for the introduction of QAS groups. The resulting QAS-modified polysiloxanes used as additive during the compounding of a silicone mastic confer to it excellent bactericidal properties that are retained after a 2-month contact with water. These results confirm that semi-IPNs consisting of a macromolecular biocide in a polymer network are an interesting solution when long-term protection against micro-organism growth is needed with a minimum release of toxic compounds in the surrounding medium. These kind of compounds avoid the drawbacks of the protection by small molecules (active by diffusion) and those due to the covalently bound biocidal polymers (active by contact). The mixed concept of IPNs allows for a fine tuning of the two modes of action by changing the molecular weight and the hydrophilicity of the additive, its degree of immiscibility with the matrix, the density of the network, etc. We are currently investigating these various possibilities.

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