# Biocidal Polymers Active by Contact. II. Biological Evaluation of Polyurethane Coatings with Pendant Quaternary Ammonium Salts

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SYNOPSIS

Films of polyurethane were prepared by reaction of hydroxytelechelic polybutadienes carrying covalently bound quaternary ammonium salts with an aliphatic triisocyanate. These coatings exhibited high biocidal activity against Gram-positive and Gram-negative bacteria, yeasts, and moulds. It was found that many parameters controlled the bioactivity such as the time of contact between films and bacteria, the [NCO]/[OH] ratio used to prepare the cured polyurethane, the concentration of quaternary ammonium salts in the coating, and the length of the alkyl chain from $C_8$ to $C_{16}$ linked to the quaternary nitrogen atom. A secondary phenomenon of diffusion only observed with the shorter alkyl chains ($C_8$ and $C_{10}$) was shown to be due to synthesis residues. After these water-soluble impurities are eliminated, the biocidal activity remains excellent: then it is due only to a contact polymer bacteria. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Biocidal coatings are widely used to prevent the growth of microorganisms on the surface of materials (e.g., antifouling paints used to protect submerged structures in sea water). At the present time, the protection is achieved by leaching of bioactive molecules from the coating. However, these molecules are highly toxic to the environment and the protection is short-lived due to the difficulty of controlling the rate of diffusion.

To overcome these problems, anchoring the toxic compounds to a polymer backbone by a covalent nonhydrolysable bond might be a solution. In this case, the biocidal groups must act by contact with the cell membrane of the microorganisms. Quaternary ammonium salts (QAS) containing at least a long alkyl chain (at least eight carbon atoms) are good candidates for this function, because they are known to be effective against a large spectrum of microorganisms such as bacteria, algae, fungi, etc. Their mode of lethal action is postulated to involve a contact with the cell membrane.[1-3] Though the exact mechanism is not established, it is accepted that at first there is an adsorption onto the negatively charged cell surface by electrostatic interaction. Then, the long lipophilic chain diffuses through the cell wall. This leads to a weakening of the cytoplasmic membrane that causes a loss of cytoplasmic constituents and the death of the cell.

To prove the validity of this new concept, we have grafted onto hydroxytelechelic polybutadienes lateral chains ended with suitable QAS[4] and incorporated these polymers in polyurethane films. This paper reports on the biocidal properties of these new materials. The properties were evaluated by contact and by diffusion (see EXPERIMENTAL). Both methods were used jointly to demonstrate that the activity is only due to a contact of the microorganism with the polymer *in the absence of diffusion of any toxic substance.*

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## EXPERIMENTAL

### Reactants

HPB1 and HPB2 are commercial products from Atochem (Polybd R45HT) and from Nippon Soda (G1000), respectively.

*N,N*-Dimethylamino *N*-propyl-tetramethyldisiloxane (AS1) was prepared from allyl dimethylamine and 1,1,3,3-tetramethyldisiloxane ($M'_2$) (a Jansen product distilled before use) according to a procedure described elsewhere.[4] *N,N*-Dibutylamino *N*-propyltetramethyldisiloxane (AS3) was prepared similarly from allyl dibutylamine. *N,N*-Dimethylamino *N*-propyltetramethyltetrasiloxane (AS2) was obtained from 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (a Petrarch product distilled before use).

Alkyl bromides from Aldrich (purity > 99%) were distilled before use.

Polyisocyanate is an aliphatic biuret triisocyanate derived from hexamethylene diisocyanate containing 22 isocyanate groups per 100 g of polymer (Tolonate HDB from Rhône–Poulenc).

### Synthesis of HPBAQ

Grafting of the aminoalkyl siloxane AS1, AS2, or AS3 on HPB1 or HPB2 was carried out by hydrosilylation according to a procedure described elsewhere.[5] HPBi modified with ASj is referred to as HPBiAj.

Pendant tertiary amino groups of HPBA were quaternized by different alkyl bromides from $C_8$ to $C_{16}$ according to a method described in a preceding paper.[4] They are referred to as $HPBAQ_n$ where $n$ is the number of carbon atoms of the alkyl bromide.

### Preparation of Polyurethane Films HPBAQPU

Cured polyurethane films (HPBAQPU) were prepared by mixing HPBAQ and Tolonate HDB in ethyl acetate. The mixture was deposited on a plate and spread with a hand-coater of 90 $\mu$m. The film was then dried for 24 h at 60°C.

### Measurements

The structure of the polymers was determined by $^1$H NMR using a Bruker ACE 200 spectrometer at 200 MHz. Molar masses were determined by GPC using a Waters GPC instrument, and by VPO with a Wescan 233100 instrument in toluene at 50°C.

### Biocidal Assessment

All procedures were carried out under aseptic conditions.

#### *Test by Contact*

Biocidal testing by the contact method was performed according to the literature.[6] The bacterial suspension containing $N_o$ bacteria was deposited on the surface (1 cm$^2$) of the film. After a determined time of contact at 20°C, the sample was washed with 100 mL of neutralized solution (Tryptone: 0.1%; NaCl: 0.8%; distilled sterile water: 98.1%). Then, tenfold dilutions were carried out from this solution adding 1 mL to 9 mL of distilled sterile water. Each dilution was filtrated on a 0.5-$\mu$m membrane in order to isolate the bacteria from the suspension. The membranes were placed on a Petri dish containing a nutrient medium (gelose) and heated at 37°C during 24 h. After this period, the surviving bacteria gave birth to colonies that were counted.

The decimal logarithm of the ratio of the initial number of bacteria $N_o$ to the number of surviving bacteria $N$ was used to express the antibacterial activity by contact of the sample (*logarithmic reduction ratio*).

#### *Test by Diffusion*

The surface of a nutrient medium (Mueller–Hinton) was seeded by a uniform layer of a bacterial suspension ($\approx$ 2.0 $10^6$ bacteria/mL). The film (1 cm$^2$) was placed facing on the bacteria. If a toxic compound leached out from the coating, the bacterial growth was inhibited around the sample. The width of this area expressed the antibacterial activity by diffusion.

## RESULTS AND DISCUSSION

### Preparation of PU Films Containing Covalently Bound QAS

The synthesis was described in the first part of this series.[4] Two types of hydroxytelechelic polybutadiene were used, HPB1 and HPB2. They differ in the content of 1,2-units, molar masses, and mean number of hydroxyl groups per molecule (Table I). QAS were grafted onto the vinylic double bonds of polybutadiene in two steps. The first step was the grafting by hydrosilylation of an aminoalkylsiloxane bearing a silane function at one extremity. Three different compounds (AS1, AS2, AS3) were synthe-

sized to study the influence of the nature of the amino group and the length of the spacer:

$$H-Si(CH_3)_2-[O-Si(CH_3)_2]_n-(CH_2)_3-NR_2$$

AS1: $n = 1$, R = Me; AS2: $n = 3$, R = Me;

AS3: $n = 1$, R = Bu.

The modified polybutadienes are denoted $HPB_iA_j$, where the index $i = 1, 2$ refers to the starting polybutadiene (HPB1 or HPB2) and $j = 1, 2, 3$ to the amine (AS1, AS2, or AS3). Their characteristics are reported in Table II. Yields of hydrosilylation were higher than 90%, but the number of OH groups decreased slightly during the reaction (20–30%). However, this effect is compensated by an increase of the molar mass of polybutadiene due to traces of 1,1,3,3-tetramethyldisiloxane used in excess in the synthesis of the aminoalkylsiloxane that was difficult to eliminate totally.[4] For instance, in the case of HPB1A1, the apparent functionality decreased from 2.5 to 1.9, but because of chain coupling, the effective number of OH per macromolecule was 3.8. The second step was the quaternization of the pendant tertiary amines by a linear 1-bromoalkane $C_nH_{2n+1}Br$ with $n = 8$, 10, 12, 14, or 16 (quaternized polymers are referred to as $HPBAQ_n$). Whatever the alkyl bromides, yields were higher than 90% and functionalities were not modified.

Polyurethane coatings were prepared by mixing $HPBAQ_n$ with an aliphatic triisocyanate (Tolonate HDB) without addition of catalyst (films are referred to as $HPBAQ_nPU$).

## Microbiological Testing

Preliminary experiments were carried out with different types of microorganisms to evaluate the spectrum of biocidal activity of the films. Table III shows that very high activities were reached (characterized by logarithmic reduction ratio higher than 6) for Gram-negative bacteria as well as Gram-positive bacteria. This result is unusual because QAS are claimed to be less active against Gram-negative bacteria that have a more resistant cell wall.[1,2] This was observed, for instance, with poly(trialkylvinylbenzylammonium) chlorides[3] in solution.

$HPBAQ_nPU$ also exhibited high activity against yeasts and mould, *Rhizopus nigricans* being a very resistant species. A similar result was recently described by Battice and Hales.[7] They prepared a trialkoxysilane carrying a QAS as a substituent, $(CH_3O)_3Si-(CH_2)_3-N^+(CH_3)_2C_{16}H_{33}, Cl^-$, that is incorporated in a polyurethane foam. The foams exhibit a broad spectrum of biocidal activity (bacteria, fungi, yeasts, and algae).

### *Time of Contact*

An important factor for the characterization of a biocidal polymer is the time of contact necessary to

**Table I Macromolecular Characteristics of Hydroxytelechelic Polybutadienes**

| HPB | 1,2 Content | $M_n$ (VPO) | OH Functionality |
|---|---|---|---|
| HPB1 | 0.2 | 2800 | 2.5 |
| HPB2 | 0.886 | 2000 | 2.0 |

**Table II Yields of Grafting by Hydrosilylation of $M'_2A$ Onto 1,2-units of HPB and OH Functionality of HPBA Prepared**

| HPBA | Modified 1,2-Units (%) | Hydrosilylation Yield (%) | Apparent OH Functionality |
|---|---|---|---|
| HPB1A1 | 0.182 | 91 | 1.9 |
| HPB1A2 | 0.187 | 93 | 2.0 |
| HPB1A3 | 0.193 | 96 | 1.9 |
| HPB2A1 | 0.862 | 97 | 1.6 |

**Table III Biocidal Activity by Contact of HPB1A1Q14PU Coatings Against Bacteria, Yeasts, and Mould**

| Microorganisms | Time of Contact (h) | $\log(N_o/N)$ |
|---|---|---|
| Bacteria | | |
| *Escherichia coli*[a] | 1 | 6.5 |
| *Proteus mirabilis*[a] | 3 | 6 |
| *Pseudomonas aeruginosa*[a] | 3 | 6 |
| *Streptococcus faecalis*[b] | 3 | 6 |
| *Staphylococcus aureus*[b] | 3 | 6 |
| Yeasts | | |
| *Rhodotorula rubra* | 1 | 5.4 |
| *Candida albicans* | 1 | 6 |
| Mould | | |
| *Rhizopus nigricans* | 1 | 1.4 |

[a] Gram negative.
[b] Gram positive.

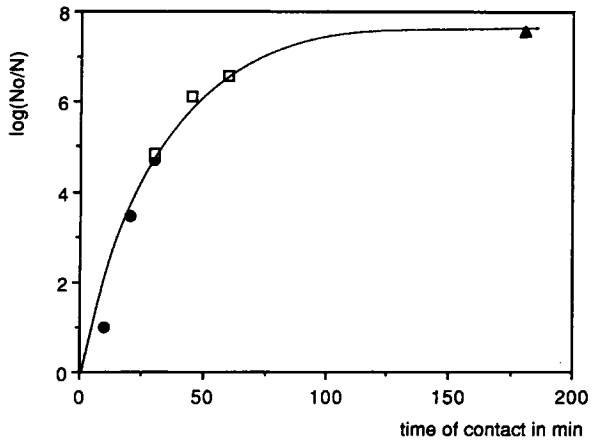



**Figure 1** Antibacterial activity of HPB1A1$Q_{12}$PU coatings versus time of contact with *Escherichia coli* ([NCO]/[OH] = 1). Initial number of bacteria: (●) $N_o$ = 2.6 $10^5$; (□) $N_o$ = 2.6 $10^7$; (▲) $N_o$ = 3.7 $10^7$.

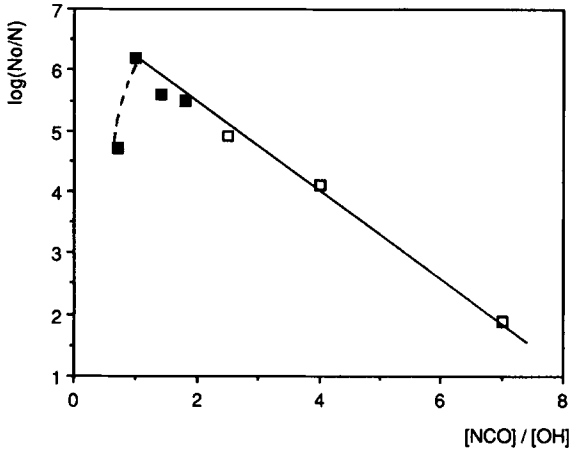



**Figure 2** Antibacterial activity of HPB1A1$Q_{12}$PU coatings versus crosslinking degree (time of contact: 1 h). Initial number of bacteria (*Escherichia coli*): (■) $N_o$ = 6.45 $10^6$; (□) $N_o$ = 6.45 $10^4$.

kill the microorganisms. Figure 1 shows a plot of the antibacterial activity of HPB1A1$Q_{12}$PU against *Escherichia coli* when a suspension of bacteria was in contact with the polymer for different times. HPB1A1$Q_{12}$PU was able to kill all the bacteria within 1 h of contact and the variation was approximately linear in the early stage. Moreover, the logarithmic activity for a given time of contact does not depend on the number of bacteria deposited on the coating (Table IV; see also Fig. 1 for results obtained with three different concentrations of bacteria). This result, which is in agreement with Kawabata et al.,[8] indicates that the destruction of microorganisms is a first-order process.

### *Influence of Ratio [NCO]/[OH]*

The conditions of preparation of HPBA$Q_n$PU are also important. The highest efficiency was obtained for a stoichiometric ratio of isocyanate and hydroxyl groups (Fig. 2). At ratios [NCO]/[OH] higher than 1, the activity strongly decreased, which may be attributed to the formation of a hard film of polyurea at the surface resulting from hydrolysis of isocyanates. This film probably hindered the accessibility of QAS to the surface. At the lowest ratios, reticulation is not complete producing sticky films that do not allow a reliable determination of the bioactivity.

**Table IV Effect of Initial Number of Bacteria Deposited on HPB1A1$Q_{12}$PU Coatings**

| | | | |
|---|---|---|---|
| Number of bacteria, $N_o$ | $2.10^3$ | $1.4.10^4$ | $1.2.10^6$ |
| Number of bacteria, $N_t$ | 5 | 30 | 2030 |
| $\log(N_o/N_t)$ | 2.6 | 2.7 | 2.8 |

[NCO]/[OH] = 1; *Escherichia coli;* time of contact: 1 h.

### *Concentration of QAS*

An important parameter controlling the bioactivity is the concentration of QAS in the coating. This effect was studied with HPB1A1$Q_{12}$ and HPB2A1$Q_{12}$ (see Tables I, II). The concentration of QAS may be changed in two ways, either by adjusting the functionalisation yield during the preparation of HPB1A1 and HPB2A1 or by diluting HPB1A1$Q_{12}$ and HPB2A1$Q_{12}$ with the corresponding unmodified polybutadiene, HPB1 or HPB2. In Figure 3, the biocidal activity of PU films prepared according to both procedures is shown as a function of the number of QAS per gram of polyurethane. As expected, the activity measured after 1 h of contact decreases with the concentration of QAS and the effect is kinetic. Indeed when the concentration of QAS is lower than the concentration used in the experiments presented in Figure 1, a time longer than 1 h may be necessary to kill the bacteria. We effectively verified that the activity of HPB1A1$Q_{12}$ diluted with HPB1 increased with time. For instance, the logarithmic reduction ratio of a PU-film prepared with a mixture HPB1A1$Q_{12}$/HPB1 containing 2.64 $10^{-4}$ QAS/g was 2.0 after 1 h and 3.2 after 2 h (test by contact, *E. coli*).

Figure 3 shows that both ways of modifying the content of QAS (dilution or partial grafting) lead to the same biocidal activity for a given HPB. Sur-

prisingly coatings based on HPB2A1$Q_{12}$ are less active than coatings based on HPB1A1$Q_{12}$ when compared at the same concentration of QAS. This may be due to the high thermoplastic character of HPB2 and a higher trend to give phase separation that contributes to the lowering of the concentration of QAS at the surface.

Biocidal activity of polyurethane films prepared from HPB1A1$Q_8$ diluted with HPB1 were also determined against a yeast (*Candida albicans*) and a mould (*Rhizopus nigricans*). In both cases (Fig. 4), the bioactivity decreased linearly with the concentration in QAS as mentioned for *E. coli*, with the observation of a threshold.

### *Influence of Alkyl Substituents of QAS*

As reported in the literature, quaternary ammonium salts possess biocidal activity when the length of at least one substituent is a long aliphatic chain containing from 8 to 16 carbon atoms.[1] To verify the effect of the chain length, HPB1A1 was quaternized with different linear alkyl bromides from $C_8$ to $C_{16}$. Biocidal activity of the corresponding films HPB1A1$Q_n$PU was determined by contact and by diffusion (Fig. 5). The bioactivity measured after 1 h of contact was practically independent of the length of the alkyl chain (Table V). However, the behaviour of the same samples in the diffusion test was very different: for chains with 12, 14, and 16 carbon atoms, the polyurethane coatings exhibited

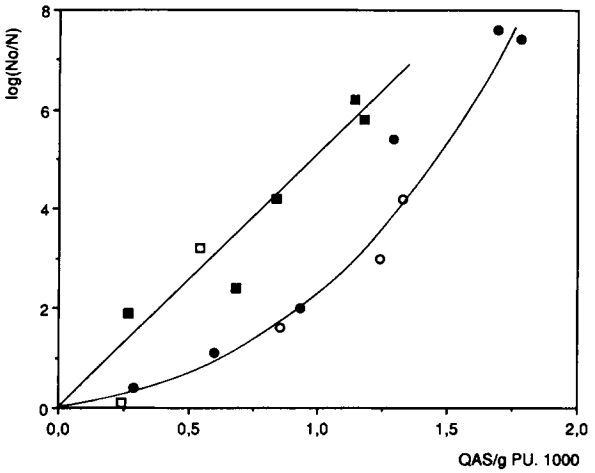



**Figure 3** Effect of QAS concentration on the antibacterial activity by contact. ([NCO]/[OH] = 1; *Escherichia coli;* time of contact: 1 h). (■) HPB1A1$Q_{12}$ incompletely grafted; (□) HPB1A1$Q_{12}$ diluted with HPBA1; (●) HPB2A1$Q_{12}$ incompletely grafted; (○) HPB2A1$Q_{12}$ diluted with HPBA2.

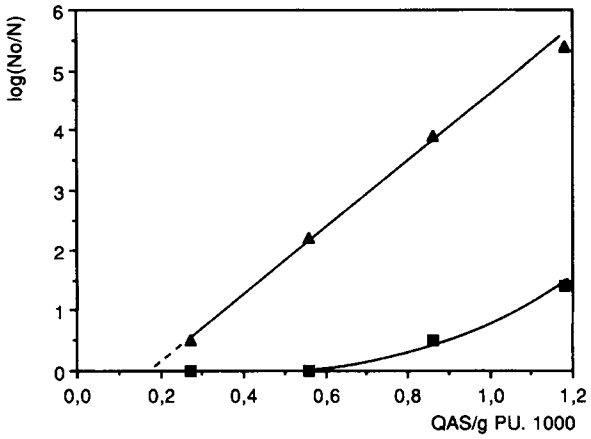



**Figure 4** Effect of QAS concentration on the biocidal activity by contact against (▲) a yeast, *Candida albicans*, and (■) a mould *Rhizopus nigricans*. HPB1A1$Q_{12}$ diluted with HPBA1; [NCO]/[OH] = 1; time of contact: 45 min.

no diffusion, whereas, for 8 and 10 carbon atoms, a zone of inhibition was observed (9 mm in the case of octyl). On the other hand, it was verified that a polyurethane coating based on unmodified HPB showed no diffusion.

We also changed the bulkiness of the substituents by replacing methyl groups with butyl groups in the case of a quaternization by octyl bromide (HPB1A3$Q_8$). The logarithmic reduction ratio was 2–3 orders lower after 1 h of contact (Table V) and the value was little improved after 2 h. This is probably due to the bulkiness of the substituents that hinder the diffusion through the cell membrane. A

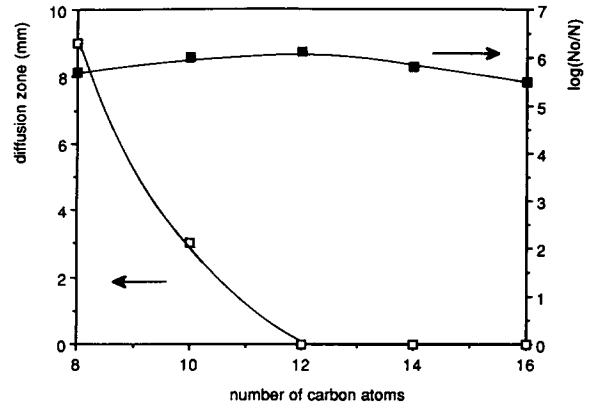



**Figure 5** Influence of the number of carbon atoms of the alkyl chain in the QAS on the antibacterial activity of HPB1A1$Q_n$PU coatings tested (■) by contact (time of contact: 1 h) and (□) by diffusion. [NCO]/[OH] = 1; *Escherichia coli.*

**Table V Logarithm of Reduction Ratio of Surviving Bacteria After Contact With PU Based on Different HPBAQ**

| PU-films Based on | $\log(N_o/N)$ |
|---|---|
| $HPB1A1Q_8$ | 5.7–6.2[a] |
| $HPB1A1Q_{10}$ | 6.0 |
| $HPB1A1Q_{12}$ | 6.1–6.4[a] |
| $HPB1A1Q_{14}$ | 5.8–6.4[a] |
| $HPB1A1Q_{16}$ | 5.5–6.0[a] |
| $HPB1A2Q_{12}$ | 2.6 |
| $HPB1A3Q_8$ | 3.1–3.6[a] |
| $HPB2A1Q_{12}$ | 7.4–7.6[a] |

*Escherichia coli*, time of contact: 1 h.
[a] Extreme values of several experiments.

similar explanation has already been proposed by Kawabata et al.[8]

The observation of a zone of inhibition for polymers quaternized with the shorter alkyl bromides means that toxicants leach out of the coating. In order to identify the molecule responsible for the diffusion, we prepared a polyurethane coating from HPB1 and Tolonate HDB containing various compounds likely to be present in HPBAQ (Table VI). No diffusion occurred with $C_8H_{17}Br$ and the aminoalkylsiloxane AS1. On the other hand, this aminoalkylsiloxane quaternized with $C_8H_{17}Br$ ($AS1Q_8$) exhibited an important activity by diffusion (7 mm) against *E. coli*. Thus $AS1Q_8$ may be responsible for the diffusion observed in the case of $HPB1A1Q_8PU$ films.

In order to accelerate the lixiviation of the biocidal organic compound contained in the coatings, a sample of $HPB1A1Q_8PU$ containing $1.144\ 10^{-3}$ QAS/g was immersed in water under stirring. The sample was periodically tested by diffusion and by contact. After 6 days of immersion in water, the zone of diffusion completely disappeared but the coating still showed a good activity by contact (logarithmic reduction ratio about 3.2, *E. coli*, 1-h contact). This value characterises the true biocidal activity by contact, in the absence of diffusion.

After complete diffusion of the water-soluble agent, the aqueous phase was evaporated. The organic residue was dried under vacuum and analyzed by $^1H$ NMR (Fig. 6). The spectrum shows the absence of signals characteristic of the doubles bonds of polybutadiene (1,4-units at 5.4 ppm), but also shows the presence of peaks corresponding to QAS (3.5 ppm) and peaks attributed to $CH_3$ and $CH_2$ linked to silicon atoms (respectively at 0.08 and 0.58 ppm). The ratio of integrations between the protons of $CH_3$—Si groups and the protons in $\alpha$ of the quaternary nitrogen atom was equal to 1.1, consistent with the following structural group:

$$Br^-,\ (CH_3)_2(C_8H_{17})N^+$$
$$—(CH_2)_3—Si(CH_3)_2—O—Si(CH_3)_2—\sim.$$

This structure suggests that the compound may be $AS1Q_8$, the presence of which is easily explained in the polymer because the yield of hydrosilylation was not complete ($\approx$ 90%, see Table II). The unreacted AS1, not eliminated during polymer precipitation, would be quaternized by RBr at the same time as the polymer.

However, the spectrum of the lixiviated compound did not show the signal characteristic of the SiH functions. These functions probably reacted with ethanol during quaternization. The resulting ethoxysilane is very sensitive to hydrolysis and leads to silanols that condensate easily in siloxane. Thus the molecule responsible for the diffusion observed in the case of $HPBAQ_8$ probably has the following structure:

**Table VI Influence of Organic Synthetic Residues Incorporated in HPB1PU Coatings on Biocidal Activity by Diffusion**

| Microorganisms | Compound Added to HPB1PU | | | | |
|---|---|---|---|---|---|
| | None | $C_8H_{17}Br$ | AS1 | $AS1Q_8$ | $AS1Q_{16}$ |
| Bacteria, *Escherichia coli* | 0 | 0 | 0 | 7 | 0 |
| Yeast, *Rhodotorula rubra* | 0 | 0 | 0 | 1 | 0 |
| Mould, *Rhizopus nigricans* | 0 | 0 | 0 | 1.5 | 0 |

Values reported in this table are measured in mm.

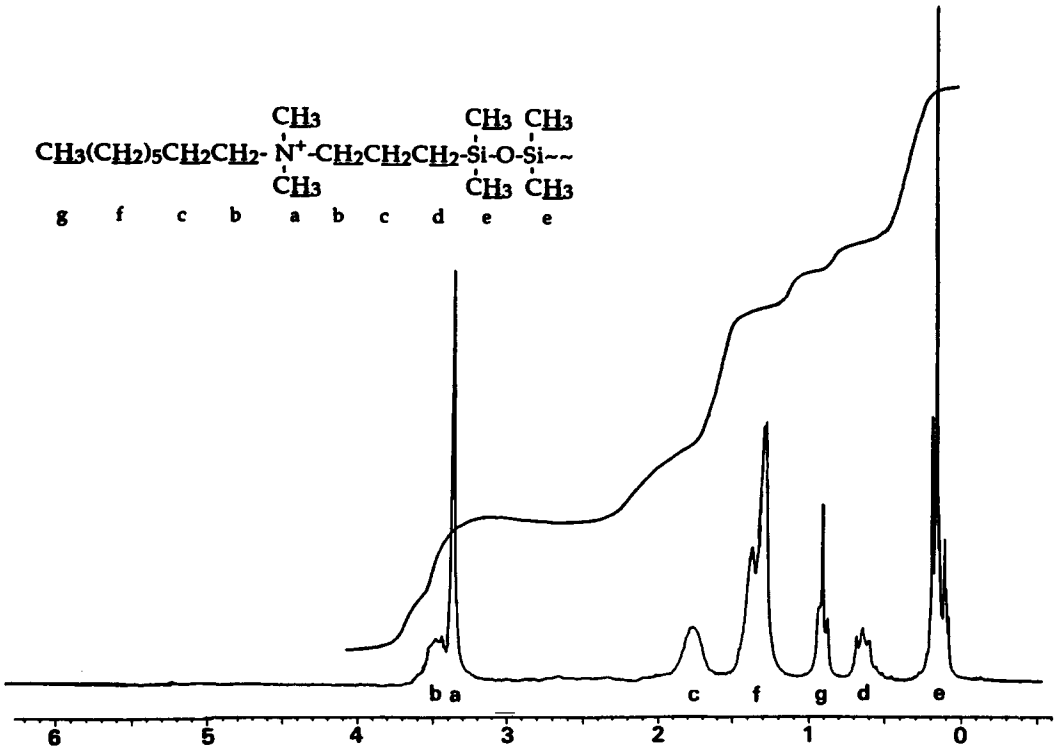
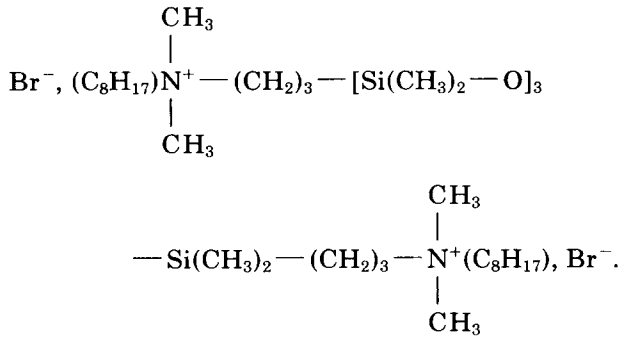



**Figure 6** 200 MHz $^1$NMR spectrum of the water soluble residue extracted from HPB1A1$Q_8$PU coatings. Solvent: $CDCl_3$; temperature: 25°C.




The absence of activity by diffusion observed with dodecyl, tetradecyl, and hexadecyl chains may be interpreted in terms of increasing hydrophobicity. When the solubility of the dication in water decreased, the rate of diffusion became probably too slow for a zone of inhibition to be observed in the diffusion test. This was verified with an authentic sample of AS1$Q_{16}$ deliberately added to a blank film of PU based on HPB1: the film did not show any measurable zone of diffusion (Table VI).

It is noteworthy that films of HPB1A1$Q_8$PU tested by the diffusion method against a yeast (*Rhodotorula rhubra*) and a mould (*Rhizopus nigricans*) showed no diffusion, whereas the same polymer presented a zone of diffusion of 9 mm in the case of *E. coli*. This is probably due to the fact that yeasts and moulds have a very high rate of growth and are able to use the dead cells as nutrients. Therefore these microorganisms are not suitable for a study of the diffusion of a biocide out of a solid.

### *Influence of Siloxanic Spacer*

The siloxanic arm was thought to favour the gathering of QAS at the surface of the film. For instance, McGrath et al.[9] have shown that the siloxane fragment of a block copolymer siloxane–urethane incorporated in a polyurethane network is mainly situated at the surface as a consequence of their low surface tension.

To check the effect, *N,N*-dimethylamino *N*-propyloctamethyltetrasiloxane (AS2) was synthesized and grafted onto HPB1 by hydrosilylation (Table II). Quaternization with dodecyl bromide (yield higher than 90%) gives a polymer referenced as HPB1A2$Q_{12}$. The PU film obtained from this polymer was tested by contact. Unfortunately, the logarithmic reduction ratio was several orders of mag-

nitude lower than the value obtained with the corresponding disiloxane (Table V). This was not easy to explain. It is possible that an increase of the length of the siloxanic arm induced a demixtion, trapping a part of the QAS in the bulk of the film and limiting their concentration at the surface.

We have also confirmed that the location of QAS at the free extremity of a flexible side chain is a very important factor. For this purpose, we prepared a polyurethane containing QAS in the main chain by reaction of *N*-benzyl-*N*-dodecyl-bis(2-hydroxyethyl) ammonium chloride with an excess of Tolonate HDB. In a second step, the remaining isocyanate functions were reacted with a polyol (Desmophen D651 from Bayer). The films tested by the contact method had no bactericidal activity. This shows that the flexibility of the siloxanic arm (and probably also its hydrophobicity) plays an important role in the efficiency of a polymer biocide active by contact. Nevertheless other polymers with QAS in the main chain (e.g., ionenes) have been claimed to possess antibacterial and antifungal activity.[10]

## CONCLUSION

A biocidal polymer for a variety of microorganisms only by contact in the absence of diffusion of any toxic substance was demonstrated. Polyurethanes based on hydroxytelechelic polybutadienes modified by grafting a QAS at the end of a spacer constituted of C—C and siloxane bonds presented a very good activity characterised by logarithmic reduction ratios higher than 6. Due to difficulties in the polymer purification, some synthesis residues were present in the polymer. These naturally water soluble and biocidal compounds are responsible for the inhibition of bacteria growth observed at a short distance around the film in diffusion tests. The concentration of these impurities is low and they are rapidly exhausted by washing. When diffusion has completely stopped, activity by contact remains at an acceptable level for practical applications (many commercial coatings tested in similar conditions have logarithmic reduction ratios around 2).

Concerning the chemical structure of the QAS, the activities were not significantly different for polymers bearing a $-N^+(CH_3)_2R$ group when R varied from $C_8H_{17}$ to $C_{16}H_{33}$. On the contrary, $-N^+(C_4H_9)_2C_8H_{17}$ was much less active than $-N^+(CH_3)_2C_8H_{17}$. This means that steric hindrance played an important role. A longer spacer based on a tetrasiloxane instead of a disiloxane caused no improvement to the biocidal activity, probably because the QAS were trapped in the bulk of the polymer.

These conclusions serve as a guide for designing new biocidal coatings that have the advantage of being nonpolluting. Ideally, the activity may be permanent because the biocidal group is not consumed during the course of interaction with microorganisms. Nevertheless, the activity may decrease with time for several reasons and the stability of the biocidal properties of HPBAQPU in environmental conditions is an important point to study. This is the subject of the next part of this series.[11]

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