Biocidal Polymers Active by Contact. III. Ageing of Biocidal Polyurethane Coatings in Water

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SYNOPSIS

Polyurethane coatings prepared from hydroxytelechelic polybutadiene with pendant quaternary ammonium salts (QAS) are able to kill microorganisms only by contact. In order to determine the time of protection against microorganisms, these biocidal polymers were submitted to various ageing conditions. The activity remained constant after exposure to a very high number of bacteria (*Escherichia coli*). Nevertheless immersion in water caused a slow decrease of activity with time whatever the QAS examined ($-N^+R_2R'$ with R = Me or Bu and R' = *n*-octyl to *n*-hexadecyl). The phenomenon can be analysed in two stages. The first one, short (5–10 days) and limited, is due to the diffusion of a water-soluble synthesis residue. At the end of this period, the samples are still active and the activity is only due to a contact polymer–bacteria. The second stage is much slower and is accompanied by a transformation of QAS in amine. This is attributed to an equilibrium between QAS, amine, and alkyl bromide slowly shifted toward the formation of amine because of a weak solubility of alkyl bromide in water. Increasing the lipophilicity and bulkiness of the QAS substituents improves the durability of the biocidal activity. Some samples still exhibit a good activity after more than 1 year of ageing in harsh conditions.
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INTRODUCTION

Quaternary ammonium salts (QAS) possessing at least one alkyl substituent of at least eight carbon atoms[1] are able to kill microorganisms such as bacteria, fungi, and moulds by interacting with the cell membrane.[2] QAS of low molar mass are widely used as "cationic disinfectants." Water-soluble polymers bearing QAS as lateral groups linked through non-hydrolysable covalent bonds exhibit bactericidal and fungicidal activity.[3,4] It has been shown that insoluble polymers containing the same type of QAS are also efficient in the solid state.[5-7] In the preceding papers of this series, the synthesis of hydroxytelechelic polybutadienes bearing QAS at the extremity of a siloxanic side chain were described[8] and the biocidal properties of PU-films based on these polyols were studied.[9] The coatings present a good efficiency against Gram-positive and Gram-negative bacteria, yeasts, and moulds. Correlations between tests by contact and tests by diffusion allowed us to demonstrate that the films are effectively active by a simple contact polymer–bacteria without liberation of any toxic compound (except for a small amount of a water-soluble synthesis residue easily eliminated by washing).

These polymers have potential applications as coatings in many domains such as food manufacturing, building trades, or marine paints as long as the material retains its biocidal properties as well as its physical and mechanical properties for a time at least comparable to the lifetime of classical binders. Many parameters may influence the biocidal activity: modification of the biocidal group during interaction with bacteria, acidity or basicity of the medium, hardness of water, UV radiations, adsorption of organic products, etc. Very few studies have been performed on the influence of ageing on the biological properties of QAS-grafted polymers. Polyvinylchloride coatings with pendant QAS that

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present good antifouling properties in sea water[6] become inactive after a few months. Textile fibers treated with 3-(trimethoxysilyl)propyldimethyloctadecylammonium chloride show high algicidal activity; the property was maintained during about 10 washings but decreased after the eleventh.[7] The authors suggested that QAS could be hidden by the dead algae.

This paper reports two series of experiments intended to estimate the durability of the protection against microorganisms of various QAS-carrying polyurethanes in water, in the presence, or in the absence of bacteria. The first series consisted of repeated contact of the samples with large numbers of bacteria; the second series was carried out by immersing the samples in pure water either under vigourous mechanical stirring (dynamic conditions) or in static conditions. The biocidal activity was determined at intervals by two methods: a test by contact for the determination of the *logarithmic reduction ratio* (decimal logarithm of the ratio of the initial number of bacteria to the number of survivors after a given time of contact) and a test by diffusion for the detection of biocides able to migrate out.[9]

EXPERIMENTAL

Materials

Hydroxytelechelic polybutadiene referred to as HPB1 is a commercial product from Atochem (Polybd 45HT). Grafting *N,N*-dimethylamino *N*-propyltetramethyldisiloxane (AS1) or *N,N*-dibutylamino *N*-propyltetramethyldisiloxane (AS3) onto the 1,2-units of HPB1 was carried out by hydrosilylation as previously described.[8]

Quaternization of the pendant tertiary amino groups by alkyl bromide was carried out in ethanol in the case of the dimethylamino derivative and in nitrobenzene in the case of the dibutylamino derivative.[8]

Polyurethane coatings were prepared by mixing $HPBAQ_n$ and an aliphatic polyisocyanate from Rhône-Poulenc company (Tolonate HDB) at a ratio [NCO]/[OH] = 1.[9]

Dimethyldodecylbenzylammonium bromide (DMDBQA) was prepared by heating an equimolar mixture of dimethyldodecylamine and benzyl bromide in ethanol for 78 h. DMDBQA was purified by crystallization in ether and dried under vacuum at 50°C for 48 h.

^{1}HNMR spectra have been performed on a Bruker ACE200 spectrometer at 200 MHz.

Biocidal Assessment

Biocidal tests by contact and by diffusion were performed according to procedures described in the preceding paper of this series.[9]

RESULTS AND DISCUSSION

The synthesis of hydroxytelechelic polybutadienes carrying covalently bound QAS was described in a preceding paper.[8] The polymers used in the present study are derived from HPB1A1 and HPB1A3, that is, hydroxytelechelic polybutadiene HPB1 (20% 1,2-units, M_n = 2800, 2.5 OH per mole) grafted either with *N,N*-dimethylamino *N*-propyltetramethyldisiloxane (AS1) or with *N,N*-dibutylamino *N*-propyltetramethyldisiloxane (AS3). According to our notation,[9] polymers quaternized with $C_nH_{2n+1}Br$ are referred to as $HPBAQ_n$ and the corresponding polyurethane films as $HPBAQ_nPU$.

Ageing in Presence of Bacteria

Kawabata and Nishigushi[4] observed in the case of soluble pyridinium-type polymers that the lethal activity becomes slower when the contact with bacteria is prolonged. In some cases, the activity stops completely. This phenomenon was interpreted by an adsorption of the polymer onto bacterial cells.

In order to check this assumption, we carried out an experiment in which a concentrated bacterial suspension (1.2 10^7 *Escherichia coli*) was deposited on a sample of $HPB1A1Q_{12}PU$ (1 cm^2). After 1-h contact at 20°C, the sample was carefully rinsed with sterile water (avoiding mechanical swipping) and submitted to a new contact with a bacterial suspension. The same procedure was repeated five times and the number of surviving bacteria determined after each run. The activity remained very high and approximately constant, which means that the polymer surface was not deactivated by contact with bacteria (Table I).

However, in the case of a crosslinked polymer such as HPBAQPU, it was difficult to be sure that the QAS was not modified after contact with bacteria. To answer this question, attempts were made with a water-soluble QAS. Dimethyldodecylbenzylammonium bromide (DMDBQA) was synthesized for this purpose because the aromatic ring could be easily detected by ^{1}H NMR. The biocidal activity of a dilute aqueous solution of DMDBQA was determined after successive additions of bacteria (Table

Table I Effect of Successive Additions of Bacteria (*Escherichia coli*) on a Sample of HPB1A1Q_{12}PU

Run Number	Time of Contact (h)	Number of Surviving Bacteria	$\log(N_o/N)$
1	1	23	5.7
2	1	41	5.5
3	1	35	5.5
4	2	0	> 7
5	2	10	6.1

$N_o = 1.2\ 10^7$ bacteria for each addition.

II). After each addition, the bacteria were let in contact with DMDBQA for 1 h at 20°C. Then the suspension was filtered with a 0.5-μm membrane and the filter was incubated at 37°C for 24 h. After the first four additions, all bacteria were killed. After the fifth addition, the efficiency seemed to decrease slightly (log reduction ratio 1.2), but this was probably due to a time of contact too short (1 h) to kill the very large number of bacteria used in this run (10^9).

After the fifth addition, the suspension containing DMDBQA was filtered to eliminate the bacteria and the filtrate was evaporated. The residue was analysed by ^{1}H NMR and identified as pure DMDBQA without any additional peak that could be attributed to bacteria decomposition products. The compound was dissolved again in water and its antimicrobial activity was tested twice against *E. coli* (Table II). The efficiency was again 100%, which means that the biocidal group retained its activity after interaction with a very high number of bacteria ($4.0\ 10^9$ as a whole).

However, the weight of DMDBQA recovered from the filtrate represented only 68% of the initial weight, which did not exclude the possibility that a part of the QAS remained adsorbed on the bacteria. Consequently, the products deposited on the filtration membrane were dried and examined by ^{1}H NMR. The spectrum was very complex, but the total absence of aromatic protons at 7.4–7.7 ppm showed clearly that the substance did not contain DMDBQA. Thus in this experiment the loss of QAS was probably due only to the experimental procedure (filtration and evaporation of minute samples), which indicates that there is no deactivation of QAS by bacteria constituents.

Ageing in Water

Samples were immersed in distilled water at 20°C in static and dynamic conditions. The antimicrobial activity against *E. coli* was determined at intervals by the method of contact. Whatever the nature of QAS and the experimental conditions, a decrease of activity was observed (Figs. 1, 2).

In all cases, the decrease of activity proceeded in two stages: Stage I, rapid and limited to a few days; and Stage II, much slower, which depends on the alkyl bromide used for quaternization. In the case of HPB1A1Q_8PU and HPB1A1Q_{12}PU, the activity falls to zero after 13 and 34 days, respectively, in stirred water (Fig. 1). For HPB1A1Q_{14}PU and HPB1A1Q_{16}PU, the activity decreased much more slowly, the samples still showing a logarithmic reduction ratio of about 1 after 1 year of immersion in stirred water (Fig. 2).

Stage I

This period is characterized by the diffusion of a water-soluble biocidal substance clearly shown by diffusion tests in the case of HPB1A1Q_8PU and HPB1A1Q_{12}PU. At the end of this period (about 5 days in the case of HPB1A1Q_8PU), the zone of inhibition completely disappeared. We demonstrated in a preceding paper[9] that the lixiviation of a soluble organic compound was responsible for this transitory phenomenon. This compound was identified as a nonmacromolecular QAS formed during the synthesis and not eliminated, namely AS1Q_n resulting from the quaternization of aminoalkylsiloxane AS1.

A rapid and limited decrease of activity was al-

Table II Biocidal Efficiency of an Aqueous Solution of Dimethyldodecylbenzylammonium Bromide DMDBQA ($2.7\ 10^{-4}$ mol/L) Against *Escherichia coli* After Successive Additions of Bacteria

Run Number	Number of Added Bacteria	Total Bacteria	Killed Bacteria (%)
1	$6.0\ 10^8$	$6.0\ 10^8$	100
2	$7.3\ 10^8$	$13.3\ 10^8$	100
3	$6.7\ 10^8$	$20.0\ 10^8$	100
4	$6.7\ 10^8$	$26.7\ 10^8$	100
5	$10\ 10^8$	$36.7\ 10^8$	93.5
6	$1.6\ 10^8$	$38.3\ 10^8$	100
7	$1.6\ 10^8$	$39.9\ 10^8$	100

Time of contact: 1 h.

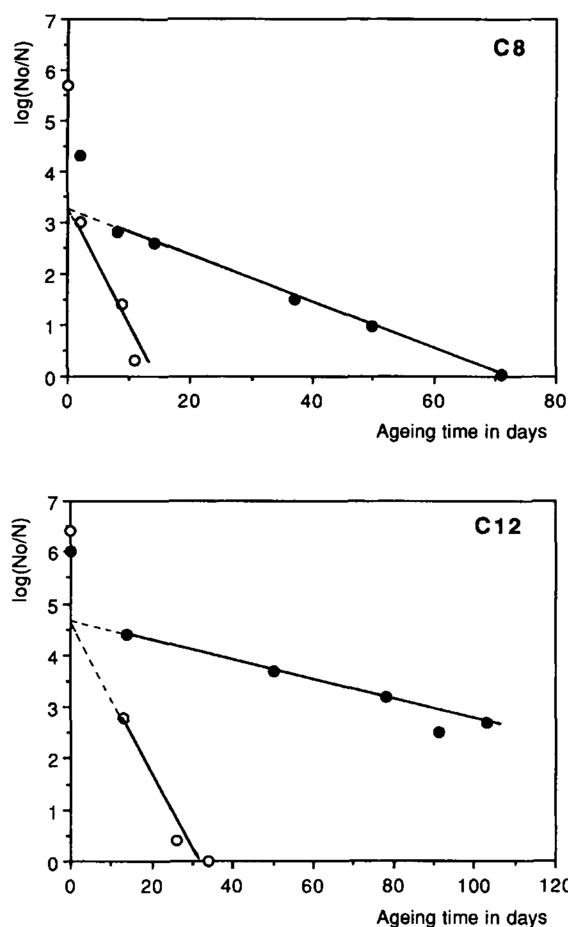


Figure 1 Variation of the antibacterial activity of HPB1A1Q$_8$PU and HPB1A1Q$_{12}$PU coatings after immersion in water, in (●) static or (○) dynamic conditions. ([NCO]/[OH] = 1; test by contact, *Escherichia coli*, time of contact: 1 h).

so observed in the case of HPB1A1Q$_{14}$PU and HPB1A1Q$_{16}$PU although no inhibition zone could be observed in diffusion tests carried out with these films. It should be linked to the leaching out of the corresponding quaternized aminoalkylsiloxanes, AS1Q$_{14}$ and AS1Q$_{16}$, respectively. The solubility of these compounds was probably so weak that the diffusion test failed to detect them. Nevertheless a part of the initial activity in contact tests should be attributed to a nongrafted QAS.

Stage II

Stage II is much slower than Stage I particularly for HPB1A1Q$_{14}$PU and HPB1A1Q$_{16}$PU (Fig. 2). With HPB1A1Q$_{16}$PU, a logarithmic reduction ratio of 1.4 was still measured after 1 year of immersion in stirred water. During this stage, the activity is only due to a contact polymer–bacteria because diffusion is no longer observed even in the case of HPB1A1Q$_8$PU and HPB1A1Q$_{12}$PU.

The decrease of activity during Stage II was approximately linear and easily extrapolated to zero time. The extrapolated value of the logarithmic reduction ratio allows the true biocidal activity by contact to be evaluated independently of the activity by diffusion interfering during the first days (Table III). The values are about 3.5 and seem to be independent of the length of the alkyl chain between C_8H_{17} and $C_{16}H_{33}$.

On the contrary, the rate of activity loss depended strongly on the alkyl chain length as indicated by the slopes of the linear parts in Figures 1 and 2 (Table III). For instance, HPB1A1Q$_{16}$PU appeared to be about 50 times more stable than HPB1A1Q$_8$PU

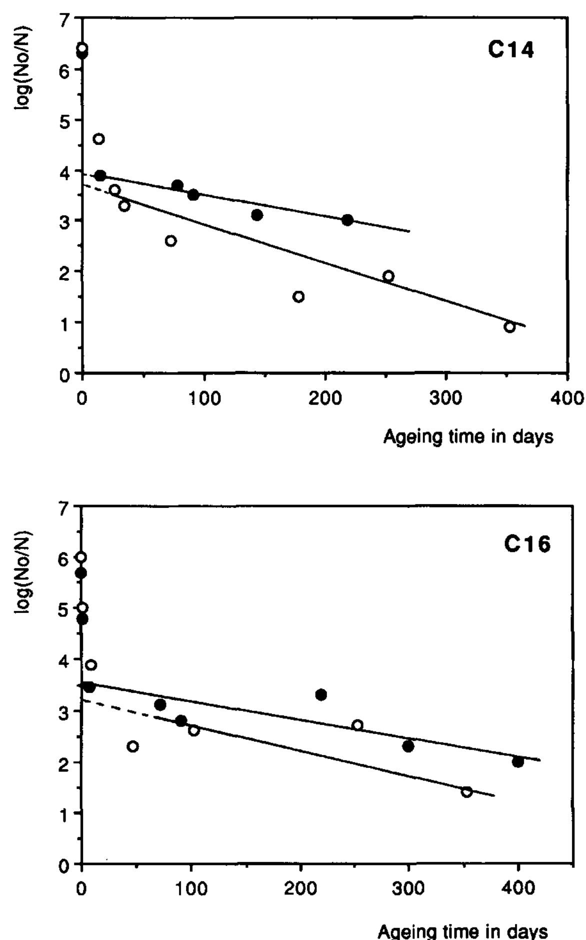


Figure 2 Variation of the antibacterial activity of HPB1A1Q$_{14}$PU and HPB1A1Q$_{16}$PU coatings after immersion in water, in (●) static or (○) dynamic conditions. ([NCO]/[OH] = 1; test by contact, *Escherichia coli*, time of contact: 1 h).

Table III Rate of Biocidal Activity Loss During Stage II in Static and Dynamic Conditions

QAS Substituents in $HPBAQ_nPU$	Initial Biocidal Activity by Contact $\log(N_o/N)_{t=0}$	Activity Loss During Stage II	
		In *Static* Water (log Unit/Day)	In *Stirred* Water (log Unit/Day)
$—N^+(CH_3)_2C_8H_{17}$	3.3[a]	4.6 10^{-2}	2.5 10^{-1}
$—N^+(CH_3)_2C_{12}H_{25}$	4.6[a]	2.1 10^{-2}	1.4 10^{-1}
$—N^+(CH_3)_2C_{14}H_{29}$	3.8[a]	3.1 10^{-3}	7.3 10^{-3}
$—N^+(CH_3)_2C_{16}H_{33}$	3.4[a]	3.3 10^{-3}	4.5 10^{-3}
$—N^+(C_4H_9)_2C_8H_{17}$	1.4[b]	—	4.2 10^{-3}

[a] Extrapolation at initial time of the linear decrease during Stage II in static and dynamic conditions (see Figs. 1, 2).
[b] Extrapolation at initial time of the linear decrease during Stage II in static conditions (see Fig. 6).

in stirred water. The experimental conditions also played an important role. For instance, in the case of $HPB1A1Q_8PU$, the sample became inactive after 70 days in static conditions, but was inactive after 10 days only when submitted to vigorous stirring. It is noteworthy that the difference between the rates of activity loss in dynamic and static conditions was smaller for the longer alkyl chains (Table III).

Causes of Activity Loss in Water

The loss of biocidal activity should be related to a chemical modification of the polymer. To study this aspect, we did not use cured films of $HPB1A1Q_8PU$, but the modified polybutadiene $HPB1A1Q_8$ itself because its solubility in organic solvents provides easier chemical analysis. Octyl substituent was chosen because the loss of activity of the corresponding PU film was particularly important (Fig. 1). A sample of $HPB1A1Q_8$ was immersed in water (where it is insoluble). At intervals, the water-soluble organic residue and the polymer were recovered separately and analysed by ^1H NMR.

The organic residue dissolved in water during the first days was shown to be a QAS containing one disiloxane group and no polybutadiene fragment. This compound could be identified as the quaternized aminoalkylsiloxane $AS1Q_8$ in agreement with the results of previous experiments carried out with cured films of $HPB1A1Q_8PU$.[9] This confirms the origin of the loss of activity observed during Stage I. It is noteworthy that $AS1Q_8$ was completely eliminated in about 5 days in stirred water, a time corresponding roughly to the end of Stage I with $HPB1A1Q_8PU$ (see Fig. 1) and to the time after which there is no more inhibition zone in the diffusion test.[9] Thus the diffusion rate is nearly the same for uncured polybutadiene ($HPB1A1Q_8$) and for the corresponding crosslinked PU-coatings ($HPB1A1Q_8PU$). The formation of a network did not seem to significantly delay the migration of the molecule. This was probably due to the low density of crosslinks.

The composition of the polymer was also followed by NMR as a function of the immersion time (Fig. 3). During the first days, the presence in the polymer of a small amount of quaternized aminosiloxane $AS1Q_8$ was confirmed by the content of 1,4-units apparently slightly higher than the initial content in HPB1.[8] After a few days, the elimination of the water-soluble $AS1Q_8$ was complete and the content of 1,4-units settled to the theoretical value (0.8).

The siloxane content of the polymer remained constant indicating no cleavage of the siloxanic bond. Nevertheless, the signal at 3.4 ppm characteristic of QAS decreases slowly and the signal at

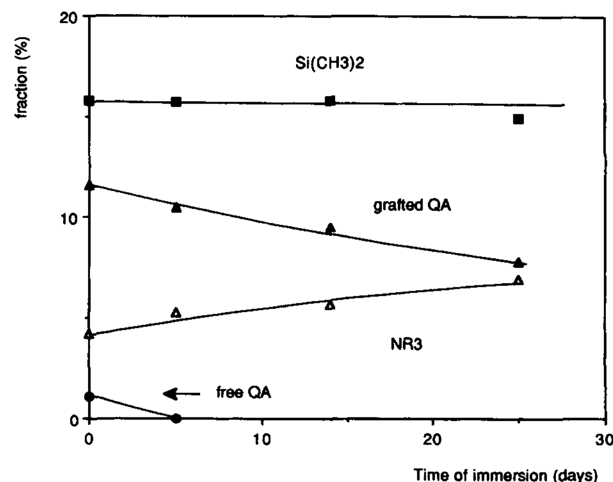
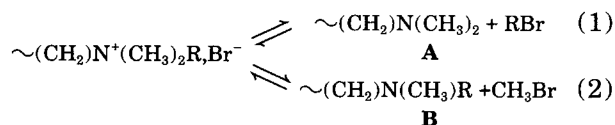


Figure 3 Composition of $HPB1A1Q_8$ determined by ^1H NMR as a function of the time of immersion in water.

2.1 ppm characteristic of the corresponding tertiary amine increases (Fig. 3), the sum of QAS and amine being constant in mole fraction and approximately equal to the mole fraction of the disiloxane groups.

The rate of degradation was somewhat nonreproducible. In some runs, as for the polymer analysed in Figure 3, the decrease was slow and regular. Sometimes, the transformation was much faster. For instance, Figure 4 shows the ^1H NMR spectrum of a HPB1A1Q_8 sample after 21 days in water. It may be seen that the signal corresponding to QAS (3.4 ppm) almost disappeared whereas the signal at 2.1 ppm (tertiary amine) was very intense.

The mechanism of this degradation was unlikely the Hoffman elimination because this reaction occurs mainly in the case of OH^- counter-ion at high temperature.[10] Most probably, we have to consider the following equilibria:



In solution, the amounts of amine and alkyl bromide should be very low at equilibrium, but in the case of QAS linked to an insoluble polymer, equilibria (1) and (2) may be continuously shifted toward the formation of amine by the diffusion of alkyl bromide. The rate of shifting depended on the solubility of alkyl bromide in water and readily decreased with the length of the alkyl chain. For instance, the solubility of methyl bromide is 1.75 g/dl whereas that of n-pentyl bromide is only 0.0127 g/dl, so that equilibrium (2) seemed *a priori* much more probable than equilibrium (1).

However, this was not confirmed by NMR analysis of the polymer (Fig. 4). From the integrations (siloxane groups at 0.08 ppm, methyl group of the alkyl chain at 0.8 ppm, and protons in α of the quaternary nitrogen at 3.2–3.6 ppm), the proportions of QAS (26.1%), amine A (34.5%), and amine B (39.5%) can be estimated. The proportion of amine A should have been much smaller if the phenomenon was only driven by the solubility of the alkyl bromide in water. It is necessary to suppose that other effects took place (steric effects, strengths of N—C chemical bonds, etc).

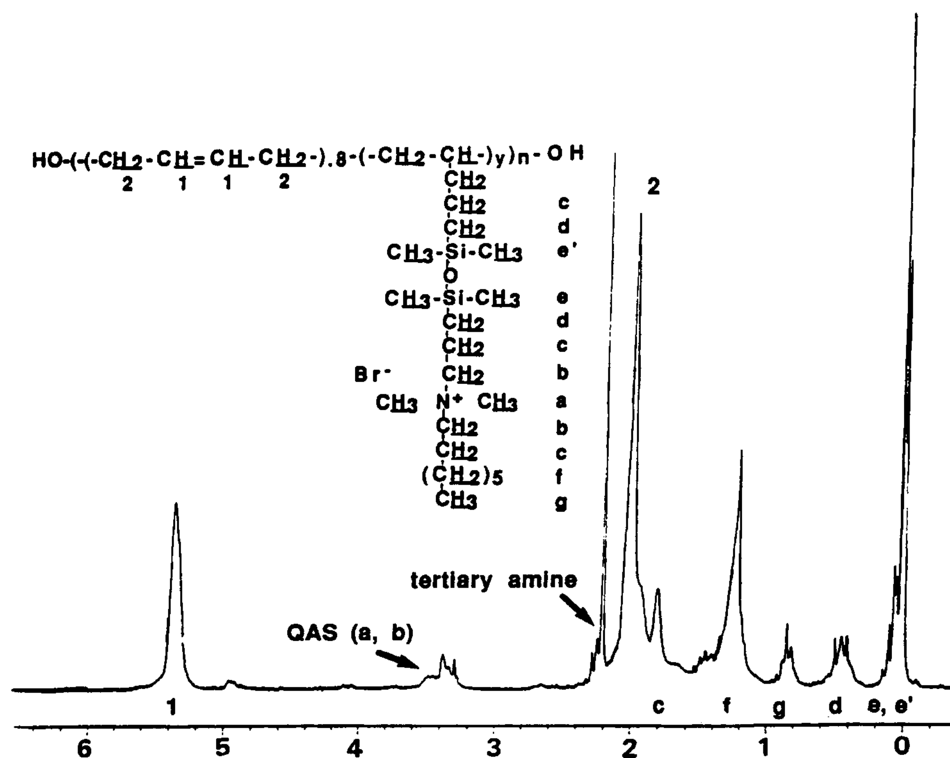


Figure 4 200 MHz ^1H NMR spectrum of HPB1A1Q8 after 21 days in water (solvent: $CDCl_3$).

Dibutyl Octyl QAS

Because the rate of loss of activity was related to an equilibrium QAS-amine and because the equilibrium was strongly dependent on the nature of the alkyl substituents, we were interested in the replacement of the methyl groups by bulkier groups (corresponding also to less soluble alkyl bromides). A number of experiments were carried out with a polybutadiene carrying $—N^+(C_4H_9)_2C_8H_{17}$, Br^- groups ($HPB1A3Q_8$). The initial biocidal activity of the corresponding PU-films ($HPB1A3Q_8PU$) was lower than that of $HPB1A1Q_8PU$ (logarithmic reduction ratio of 3.6 instead of 6).

As in the case of $HPB1A1Q_8$, an organic compound soluble in water containing no polybutadiene fragment was extracted from $HPB1A3Q_8$. This molecule was identified by NMR as $AS3Q_8$ (the unreacted amine AS3 quaternized by octyl bromide).

The variation of composition of $HPB1A3Q_8$ was determined by ^1H NMR after different times of immersion in water (Fig. 5). The presence of $AS3Q_8$ was confirmed. It is noteworthy that the diffusion of this compound was extremely slow because it was not totally eliminated after 25 days in water. Butyl group hydrophobicity can easily explain this phenomenon. As in the case of $HPB1A1Q_8$, the siloxane groups remained constant. The QAS content decreased slightly during 5 days and approximately stabilized whereas amino group content does not vary significantly during the experiment. It seems that QAS with butyl groups were more stable than with methyl groups. This was confirmed by biocidal activity measurements. The activity loss was 60 times slower in the case of $—N^+(C_4H_9)_2C_8H_{17}$ than in the case of $—N^+(CH_3)_2C_8H_{17}$ (Table I), so that $HPB1A3Q_8PU$ was still active after 110 days in stirred water (log reduction ratio 1.0) whereas $HPB1A1Q_8PU$ became inactive after 13 days in the same conditions (Fig. 6).

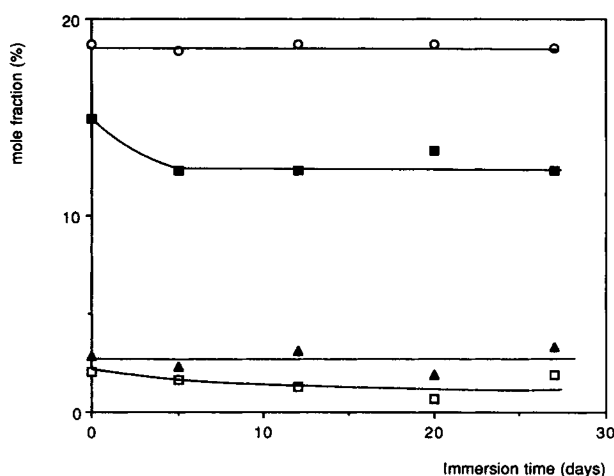


Figure 5 Composition of $HPB1A3Q_8$ determined by ^1H NMR as a function of the time of immersion in water.

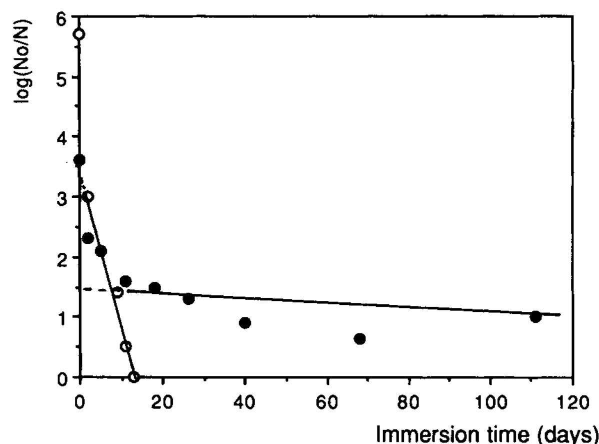


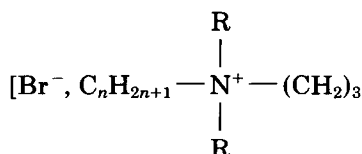
Figure 6 Comparison of the antibacterial activities of $HPB1A1Q_8PU$ and $HPB1A3Q_8PU$ coatings after immersion in stirred water ([NCO]/[OH] = 1; test by contact, *Escherichia coli*, time of contact: 1 h). (○) $HPB1A1Q_8PU$; (●) $HPB1A3Q_8PU$.

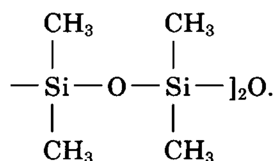
CONCLUSION

Polyurethane films based on HPBAQ constitute an effective protection against microorganism growth. QAS are active by contact in the total absence of liberation of toxic compounds when they are covalently bound to an insoluble polymer. Bacteria coming in contact with the film are killed, and apparently the dead cells do not inhibit the biocidal properties up to very high concentration, so that the lethal action may remain at its maximum efficiency even in a very contaminated environment.

However, in all cases a decrease of the bactericidal activity was observed when the samples are immersed in water. The rate of activity loss was strongly dependent on the chemical structure of the QAS substituents and on the experimental conditions. A chemical analysis coupled with microbiological tests showed that the phenomenon has two distinct origins. Both are related to a loss of QAS.

The first relatively fast phenomenon (Stage I), corresponded to the diffusion of a synthesis residue soluble in water identified by NMR as:





The diffusion rate depended on the nature of the substituents. It was much lower for R = Bu than for R = Me. In the case of HPB1A1Q_8PU or HPB1A1Q_{12}PU, Stage I is correlated to the observation of a zone of inhibition around the sample in the diffusion test. However, in the case of HPB1A1Q_{14}PU and HPB1A1Q_{16}PU, no activity by diffusion could be detected by the diffusion test.[5] This may be explained by the higher hydrophobic character of tetradecyl and hexadecyl groups.

In all cases, the logarithmic reduction ratio measured in the contact test drops to a value in the range of 3–4 when the sample is no longer active by diffusion in the diffusion test. This value may be considered as the true activity by contact.

The second stage (Stage II) was characterized by a low rate of activity loss that depends on the hydrophobic character and bulkiness of the QAS substituents. The two effects were difficult to separate. For instance, in a series of QAS of structure $N^+(CH_3)_2C_nH_{2n+1}$, an improvement of the durability by a factor 50 was obtained when n increased from 8 to 16. On the other hand, changing the methyl groups of $N^+(CH_3)_2C_8H_{17}$ by butyl groups reduced the activity loss by a factor 60, but simultaneously the initial activity by contact extrapolated to zero time is two orders lower (logarithmic reduction ratio 1.4 instead of 3.3), probably because steric crowding around the positive nitrogen hinders the interaction with the negatively charged cell surface. The best compromise seems to be obtained with $N^+(CH_3)_2C_{16}H_{33}$ for which a logarithmic reduction ratio of 2 after 400 days is measured in static conditions.

The loss of activity observed during Stage II was due to the transformation of QAS in amine as suggested by equilibria (1) and (2). These equilibria were progressively shifted to the right by solubilization of the alkyl bromide. However, the water solubility of the alkyl bromide was not the only factor governing the process. In the case of HPB1A1Q_8, amino groups $-N(CH_3)_2$ and $-N(CH_3)C_8H_{17}$ were formed approximately in equal proportion whereas, in the case of HPB1A3Q_8, the formation of both types of amino groups, $-N(C_4H_9)_2$ and $-N(C_4H_9)C_8H_{17}$, was almost negligible. It is difficult to explain why $C_8H_{17}Br$ was eliminated easily in $-N^+(CH_3)_2C_8H_{17},Br^-$ but not in the case of $-N^+(C_4H_9)_2C_8H_{17},Br^-$. This may indicate that steric hindrance around the positive nitrogen was a more important factor than the solubility of alkyl bromide.

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