

Biocidal Polymers Active by Contact. I. Synthesis of Polybutadiene with Pendant Quaternary Ammonium Groups

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SYNOPSIS

Hydroxytelechelic polybutadienes carrying covalently bound quaternary ammonium salts were successfully synthesized in three steps. The first one was the preparation of 1-(*N,N*-dimethylaminopropyl) 1,1,3,3-tetramethyldisiloxane (M_2A) by hydrosilylation. The addition occurred mainly in the terminal position of the double bond, but isomers were formed in small proportion (an isomer resulting from an inverse addition and an isomer resulting from an isomerization of the double bond). The proportion of these isomers increased with the concentration of catalyst (H_2PtCl_6). Similar results were obtained with a Pt(0)-divinyltetramethyldisiloxane complex (Pt,DVDS). The second step was the grafting of M_2A onto the 1,2-units of a hydroxytelechelic polybutadiene by hydrosilylation. The yield of the reaction was higher than 90% and the OH functionality decreased slightly. Here again, different platinum catalysts were compared: initial rates were higher with Pt,DVDS, but the final yields were better with H_2PtCl_6 . The last step was the quaternization of the pendant tertiary amino groups in methanol with alkyl bromides from $C_8H_{17}Br$ to $C_{16}H_{33}Br$. The yield of the reaction was higher than 90% and the OH functionality was not modified.

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INTRODUCTION

Coatings showing biocidal properties against microorganisms are useful in many domains such as food manufacturing, hospitals, building trades, or marine applications (antifouling paints).¹⁻³ Actually bactericidal and fungicidal properties are granted to a coating by incorporating a biocide that is slowly released. They are made in two ways:

1. A molecular biocide is simply added to a classical binder. It becomes active by migrating out of the polymer matrix.
2. A biocidal compound is grafted to a polymer by a bond sensitive to hydrolysis.

For example, organotin polymers based on acrylic

monomers are used in antifouling paints.⁴⁻⁷ The anchored biocide is released by chemical reaction with sea water. The rate of diffusion is slower than in the first case and protection is effective longer.

However, in both cases, the biocidal activity depends on the liberation of the biocide in the environment, with two consequences: a progressive loss of activity with time and a hazard to the environment (biocides are usually highly toxic).

A different approach is to bind a biocidal group to a polymer through a covalent bond that will not be cleaved in the presence of microorganisms. If the chemical groups present at the surface of the modified polymer are active by contact with the cell membrane of the microorganisms and if they are not modified during the process, a permanent activity may be expected without liberation of toxic products.

Among biocides, quaternary ammonium salts (QAS) are widely used. QAS are effective biocidal agents⁸ when one substituent is an alkyl chain with

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at least eight carbon atoms.⁹ They are claimed to cause the death of the cell by destroying the membrane integrity.¹⁰ Thus they can answer the above conditions. Nevertheless this new concept has received little attention.¹¹⁻¹² QAS have been grafted onto PVC¹¹ and coatings prepared from this polymer exhibited better biocidal properties than classical paints containing organotin compounds during 2 months in sea water, but the efficiency decreased after this period. This was probably due to a degradation of the skeleton of PVC that contained conjugated double bonds formed during the grafting of QAS. Polymers based on methacrylic derivatives of chlorophenols have been prepared for the same purpose,¹² but the biocidal activity of these materials and the absence of lixiviation have not been demonstrated.

To prepare coatings with long-term biocidal properties, we chose polyurethanes known for their good ageing characteristics in outdoor applications. QAS were introduced as lateral substituents by chemical modification of a macromolecular polyol. Hydroxytelechelic polybutadiene (HPB) containing at least two hydroxy groups per chain was chosen because the pendant vinyl groups in 1,2-units gives an addition reaction in mild conditions by hydrosilylation.

Attempts to directly graft QAS onto HPB by hydrosilylation were unsuccessful, probably because of their high hygroscopic capacity. The SiH function is sensitive to hydrolysis. For this reason, grafting was carried out in two steps: introduction of a tertiary amine quaternized later on by an alkyl bromide.

EXPERIMENTAL

Materials

N,N-Dimethylallylamine (Merck) was distilled on sodium (Eb = 63°C, GC purity > 99.9%). *N,N*-Dibutylallylamine was obtained from dibutylamine and allylbromide (2 : 1) in ethanol (24 h at 80°C). Concentrated NaOH was added to liberate the excess of dibutylamine and the mixture of secondary and tertiary amines was separated according to Hinsberg's method.¹³ *N,N*-Dibutylallylamine was finally distilled on sodium under reduced pressure (GC purity > 99%).

1,1,3,3-Tetramethyldisiloxane (Janssen) was distilled on calcium hydride before use (Eb = 70°C, GC purity > 99.9%). 1,1,3,3,5,5,7,7-Octamethyltetrasiloxane (Petrarch) was treated similarly (Eb = 170°C, GC purity ≈ 96%).

Hexachloroplatinic acid (Aldrich, purity > 99.9%) was dissolved in isopropanol (0.5 M). Pt-Divinyl-tetramethyldisiloxane complex (Petrarch) in xylene solution (0.15 M) was used as received.

Hydroxytelechelic polybutadiene HPB1 and HPB2 are commercial products from Atochem (Polybd R45HT) and HPB3 is a commercial product from Nippon Soda (G1000). In some cases, they were precipitated in methanol to eliminate antioxidant, but no difference in hydrosilylation was observed between purified and unpurified polymer.

n-Octyl bromide, *n*-decyl bromide, *n*-dodecyl bromide, and *n*-tetradecyl bromide (Aldrich) were distilled before use (GC purity > 99.9%). *n*-Hexadecyl bromide (Aldrich) was used as received (GC purity ≈ 98%).

Synthesis

Preparation of *N,N*-Dialkylaminopropylsiloxanes (*M*₂A)

N,N-Dimethylaminopropyltetramethyldisiloxane (*AS1*). *N,N*-dimethylallylamine was slowly added to a large excess of tetramethyldisiloxane in the presence of hexachloroplatinic acid at 75°C under nitrogen.¹⁴ The excess of siloxane was distilled off at atmospheric pressure. Monoadducts were then distilled under reduced pressure (yield > 90%). Three isomers were obtained in proportions depending on the conditions. The main impurity was *M*₂' (≈ 2%).

N,N-Dimethylaminopropyloctamethyltetrasiloxane (*AS2*). The compound was obtained in similar conditions (main product = 97.4%, secondary isomers = 1.7%, residual tetrasiloxane = 0.9%).

N,N-Dibutylaminopropyltetramethyldisiloxane (*AS3*). In this case, the separation of *M*₂' by distillation was complete (main product = 97.5%, secondary isomers = 2.5%).

Grafting of *M*₂A Onto HPB

The addition of *M*₂A onto the 1,2-units of HPB was carried out in hexane under reflux. Hexachloroplatinic acid and HPB were let in contact for 15 min before adding *M*₂A. The extent of reaction was followed by IR at 2120 cm⁻¹ (SiH stretching) using a Perkin-Elmer Model 580 IR spectrometer. At the end of the reaction, the modified polybutadiene (HPBA) was precipitated in methanol and dried

under vacuum. Similar results were obtained with dimethylamino and dibutylamino derivatives.

Quaternization of HPBA

In the case of dimethylamino derivatives, the reaction was carried out at 78°C in ethanol with a stoichiometric ratio of each reactant. HPBA is insoluble in ethanol contrary to HPBAQ which is soluble. Consequently, the solution became clear as the reaction progresses. At the end of the reaction, ethanol was evaporated and the polymer HPBAQ was dried under vacuum.

In the case of HPBA with dibutylamino groups, the reaction was carried out at 115°C in nitrobenzene solution during 48 h.

The yields of grafting and quaternization were determined by ¹H NMR.

Measurements

Molar masses of HPB and HPBA were measured by SEC in tetrahydrofuran with a Waters apparatus (microstyragel columns: 10⁵, 10⁴, 10³, 500, 100 Å) calibrated with standard polystyrene samples, and by VPO in toluene at 37°C (Wescan model 233).

¹H NMR spectra were performed on a Bruker ACE 200 spectrometer (200 MHz).

GC (Perkin-Elmer 8500, capillary columns; flame ionization detector) was used to follow the reaction of allyldimethylamine with M₂. Response factors of allylamine, M₂, M₂A (isomer *a*), and M₂A₂ were determined independently with respect to pyridine

(used as internal standard). The value found for isomer *a* has been attributed to isomers *b* and *c* (0.700).

RESULTS AND DISCUSSION

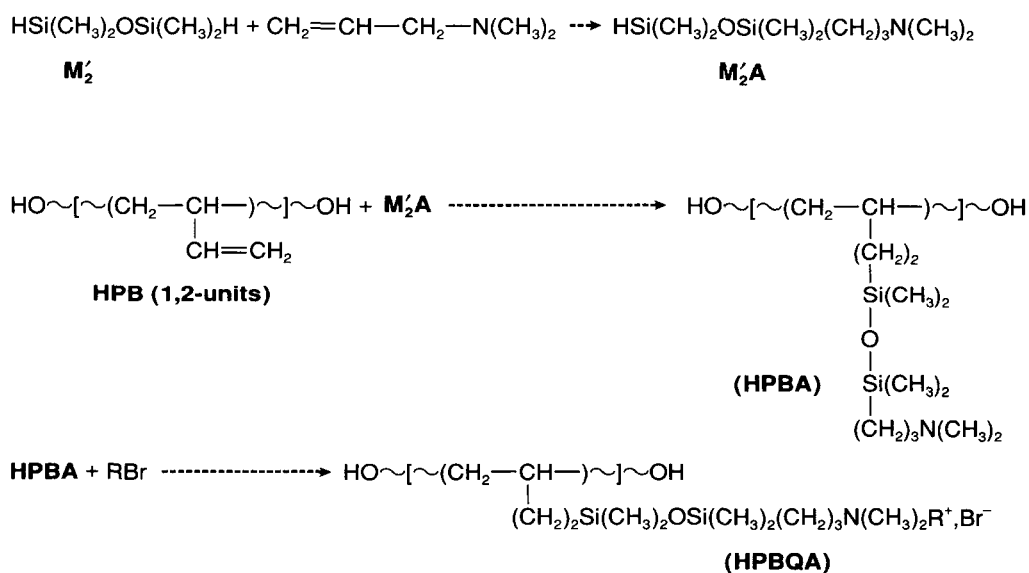
The synthesis of HPB carrying QAS side chains was carried out in three steps (Scheme 1). The first step was the preparation by hydrosilylation of a disiloxane bearing an SiH group at one end and a tertiary amine at the other end (M₂A). The aminoalkylsiloxane was then added to the vinyl groups of HPB again using hydrosilylation. The third step was the quaternization of the pendant tertiary amine by an alkyl bromide.

Preparation of 1-(*N,N*-Dimethylaminopropyl) 1,1,3,3-Tetramethyldisiloxane (M₂A)

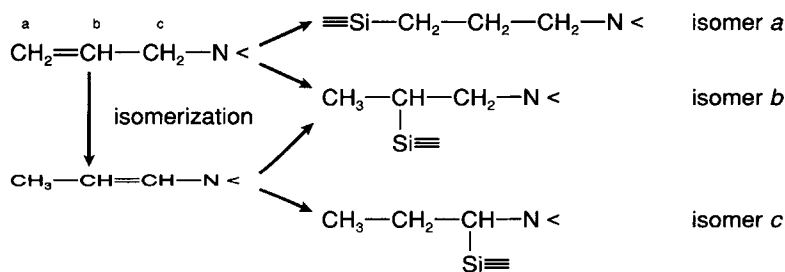
M₂A was prepared by hydrosilylation of *N,N*-dimethylallylamine (A) with 1,1,3,3-tetramethyldisiloxane (M₂) in bulk. In the literature, most catalysts of hydrosilylation are based on platinum.¹⁵ In this work, two catalysts were used and compared: hexachloroplatinic acid in isopropanol solution known as Speier's catalyst¹⁶ and a complex of Pt(0) with divinyltetramethyldisiloxane (Pt,DVDS) known as Karstedt's catalyst.¹⁷

Speier's Catalyst

A large excess of M₂ was used in order to prevent the formation of the diadduct. GC chromatograms



Scheme 1 Synthesis of HPBQA.



Scheme 2 Formation of isomers *a*, *b*, and *c*.

of the final product purified by distillation show one major peak and two small peaks of close retention times. The percentages of the three products vary with experimental conditions. For example, with a concentration in H_2PtCl_6 of $10^{-4} \text{ mol} \cdot \text{L}^{-1}$ and with a ratio $[\text{M}'_2]/[\text{A}] = 5$, the proportions are 93.4%, 3.6%, and 3.0%.

It is known that during the reaction of a silane with a vinyl group, the silicon atom adds mainly on the terminal carbon (isomer *a*), but inverse addition is also observed (isomer *b*)¹⁸ (Scheme 2). The main product has been identified as isomer *a* by ^1H NMR. The spectrum shows a singlet at 0.05 ppm [$\text{OSi}(\text{CH}_3)_2\text{-R}$], a doublet with a very small coupling constant at 0.2 ppm [$\text{OSi}(\text{CH}_3)_2\text{H}$], and a multiplet at 0.45 ppm due to a CH_2 adjacent to a silicon atom (these three peaks in a ratio 6 : 6 : 2). In addition, a small peak at 0.9 ppm may be attributed to a methyl group in β -position from a silicon atom. It is therefore characteristic of the isomer *b*.

On the other hand, hydrosilylation catalysts are able to induce isomerization of the double bond.^{19,20} In the case of *N,N*-dimethylallylamine, the formation of $\text{CH}_3\text{-CH=CH-N}(\text{CH}_3)_2$ is probably favoured by conjugation. On this compound, the silicon atom may add on both carbon atoms leading to isomers *b* and *c* (Scheme 2). Thus the formation of three isomers is expected.

The concentration of H_2PtCl_6 has an effect on the overall yield of hydrosilylation, and on the proportion of isomers. The reaction was followed by GC (see EXPERIMENTAL). Plots of the yield of hydrosilylation versus time are reported in Figure 1 for three H_2PtCl_6 concentrations. In the concentration range 10^{-3} – $10^{-4} \text{ mol} \cdot \text{L}^{-1}$, the reaction is almost complete in a few minutes. At $10^{-5} \text{ mol} \cdot \text{L}^{-1}$, the rate of reaction is much lower and the yield seems to reach a limit of around 70% after 2 h. We have shown in a preceding paper that tertiary amino groups have an inhibitory effect during hydrosilylation.¹⁴ This effect was attributed to the formation of an inactive amine–Pt complex, and the same ex-

planation holds in the present case. Consequently the catalyst concentration required to get high reaction rates and complete conversion was somewhat higher than in other hydrosilylation reactions.

In Figure 2, the percentages of secondary isomers (*b* and *c*) are plotted as a function of the extent of reaction for three catalyst concentrations. At a concentration of $10^{-5} \text{ mol} \cdot \text{L}^{-1}$, only one isomer was formed [Fig. 2(a)], whereas both isomers were observed at higher concentration [Fig. 2(b, c)]. The presence of isomer *c* implied an isomerization of the double bond (Scheme 2) and, in that case, isomers *b* and *c* were expected to be formed simultaneously. Consequently the isomer that appeared alone at low H_2PtCl_6 concentration may be identified as isomer *b* and the supplementary isomer formed at high concentration as isomer *c*. This shows that a high concentration in H_2PtCl_6 favours isomerization. Moreover, at the concentration of $10^{-3} \text{ mol} \cdot \text{L}^{-1}$, the ratio c/b was greater than 1 that means that the formation of isomer *c* from the isomerized ethylenic compound

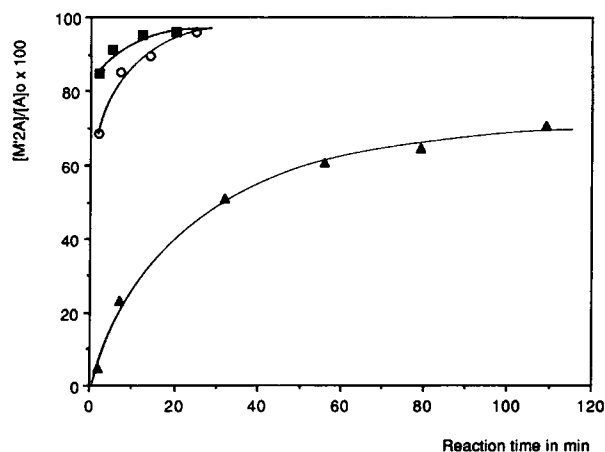


Figure 1 Effect of H_2PtCl_6 concentration on the overall yield of hydrosilylation of allyldimethylamine (A) by M'_2 . $[\text{M}'_2] = 5.02 \text{ mol} \cdot \text{L}^{-1}$; $[\text{A}] = 1 \text{ mol} \cdot \text{L}^{-1}$; temperature: 75°C . (▲) $[\text{H}_2\text{PtCl}_6]_0 = 10^{-5} \text{ mol} \cdot \text{L}^{-1}$; (○) $[\text{H}_2\text{PtCl}_6]_0 = 10^{-4} \text{ mol} \cdot \text{L}^{-1}$; (■) $[\text{H}_2\text{PtCl}_6]_0 = 10^{-3} \text{ mol} \cdot \text{L}^{-1}$.

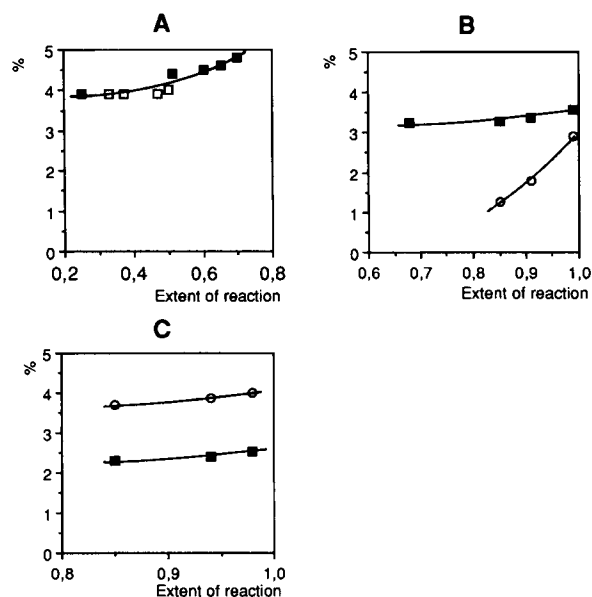


Figure 2 Influence of the catalyst on the formation of isomers (■, □) *b* and (○) *c* during hydrosilylation of allyldimethylamine (A) by M_2' . $[M_2'] = 5.02 \text{ mol} \cdot \text{L}^{-1}$; $[A] = 1 \text{ mol} \cdot \text{L}^{-1}$; temperature: 75°C . A: (■) $[H_2PtCl_6]_0 = 10^{-5} \text{ mol} \cdot \text{L}^{-1}$; (□) $[Pt, DVDS]_0 = 10^{-6} \text{ mol} \cdot \text{L}^{-1}$; B: $[H_2PtCl_6]_0 = 10^{-4} \text{ mol} \cdot \text{L}^{-1}$; C: $[H_2PtCl_6]_0 = 10^{-3} \text{ mol} \cdot \text{L}^{-1}$.

is preferred to the formation of isomer *b*. This may be due to the interaction of the nitrogen atom with the platinum atom complexed by the double bond of the isomerized form favouring the addition of hydrogen in β -position (Scheme 2).

At a ratio $[M_2']/[A] = 5$, diadducts appeared only at the end of the reaction (extent of reaction > 0.85) and their formation was limited to about 4%, whatever the catalyst concentration (Fig. 3). As expected, the percentage of diadducts increased when the ratio $[M_2']/[A]$ decreased (Fig. 4). For instance, using a ratio $[M_2']/[A] = 2$, the percentage of diadducts was already 9% for an extent of reaction of 0.82.

Karstedt's Catalyst

In the case of H_2PtCl_6 , the exact structure of the active species was not known. They were probably Pt(II) or Pt(0) derivatives depending on the concentration of the silane functions.¹⁴ It is known that Pt(0) formed *in situ* by reduction of a Pt(IV) compound by a silane exhibits a very high activity.¹⁴ On the other hand, Pt(0) complexes such as Pt(0) complexed by Pt,DVDS (Karstedt's catalyst),¹⁷ by cyclooctadiene,²¹ or by styrene²² are also very active hydrosilylation catalysts.

The activity of H_2PtCl_6 has been compared with that of Pt,DVDS in experiments carried out at two

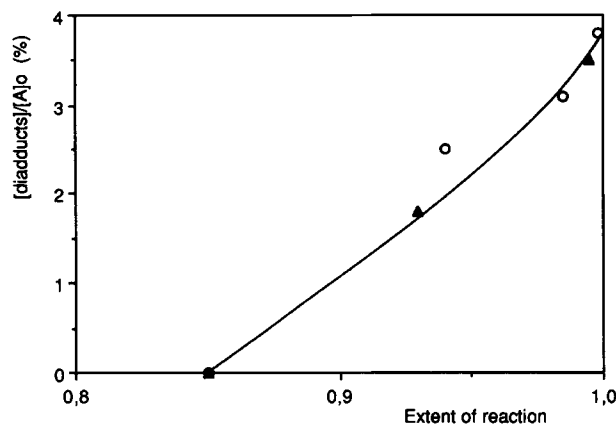


Figure 3 Effect of H_2PtCl_6 concentration on the formation of diadducts. $[M_2'] = 5.02 \text{ mol} \cdot \text{L}^{-1}$; $[A] = 1 \text{ mol} \cdot \text{L}^{-1}$; temperature: 75°C . (○) $[H_2PtCl_6]_0 = 10^{-4} \text{ mol} \cdot \text{L}^{-1}$; (▲) $[H_2PtCl_6]_0 = 10^{-3} \text{ mol} \cdot \text{L}^{-1}$.

platinum concentrations (10^{-4} and $10^{-5} \text{ mol} \cdot \text{L}^{-1}$) with each catalyst at a ratio $[M_2']/[A] = 5$ (Fig. 5). The initial rates of hydrosilylation were higher for Pt,DVDS but the catalyst turnover was not better. On the contrary, at a concentration of $10^{-5} \text{ mol} \cdot \text{L}^{-1}$, a limiting yield of 50% was obtained with Karstedt's catalyst to be compared with 70% in the case of Speier's catalyst. The inhibition of the catalyst by tertiary amino groups seems to be also effective with Pt,DVDS. The fact that H_2PtCl_6 compared satisfactorily with Pt,DVDS seems to confirm that, in the presence of an excess of silane, Speier's catalyst is reduced to an active zero-valent form of platinum, as suggested earlier.¹⁴

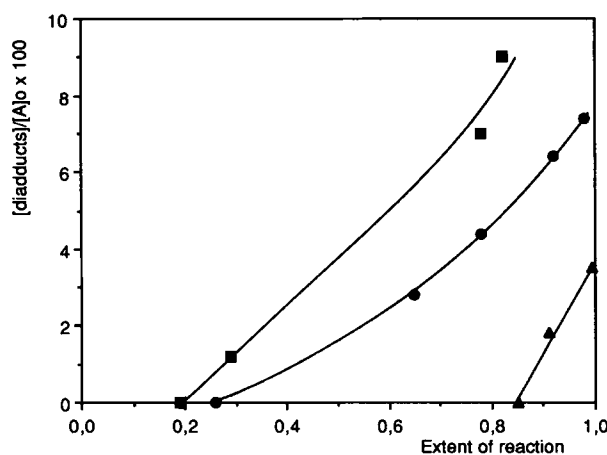


Figure 4 Influence of the ratio $[M_2']_0/[A]_0$ on the formation of diadducts. $[H_2PtCl_6]_0/[A]_0 = 10^{-4}$; temperature: 75°C . (■) $[M_2']_0/[A]_0 = 2$; (●) $[M_2']_0/[A]_0 = 3$; (▲) $[M_2']_0/[A]_0 = 5$.

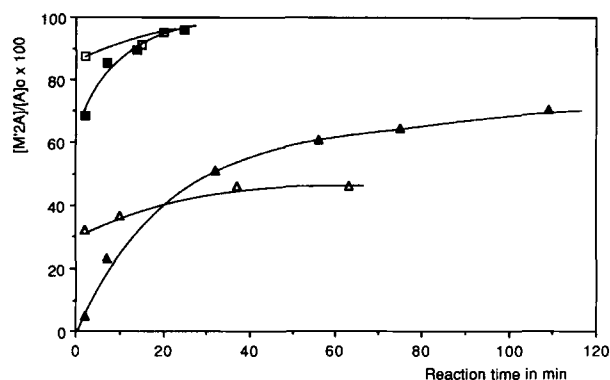


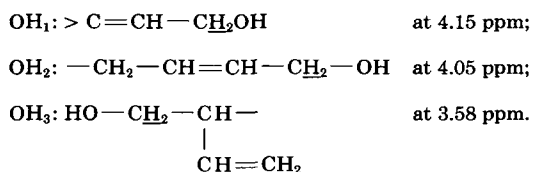
Figure 5 Catalytic activity of H_2PtCl_6 and Pt,DVDS on the kinetics of hydrosilylation of allyldimethylamine (A) by M_2 . $[\text{M}_2] = 5.02 \text{ mol}\cdot\text{L}^{-1}$; $[\text{A}] = 1 \text{ mol}\cdot\text{L}^{-1}$; temperature: 75°C . H_2PtCl_6 : (\blacktriangle) $10^{-5} \text{ mol}\cdot\text{L}^{-1}$; (\blacksquare) $10^{-4} \text{ mol}\cdot\text{L}^{-1}$; Pt,DVDS : (\triangle) $10^{-5} \text{ mol}\cdot\text{L}^{-1}$, (\square) $10^{-4} \text{ mol}\cdot\text{L}^{-1}$.

Concerning the formation of isomers *b* and *c*, no significant difference was found between the two catalysts [Fig. 2(a)]. Conflicting results have been reported in the literature concerning the capability of Pt,DVDS to suppress anomalous addition. It was found that inverse addition on a terminal $\text{C}=\text{C}$ bond was completely absent with this catalyst whereas it could reach 30% of the final products with H_2PtCl_6 .²³ On the contrary, inverse addition was found to amount to 20% during the hydrosilylation of an allylcarbonate in the case of Pt,DVDS .²⁴

Grafting of M_2A Onto HPB

Characteristics of HPB

Three commercial samples of HPB were used. Molar masses were determined by VPO and SEC. The microstructure was identified by ^1H NMR [Fig. 6(a)]. The content in 1,2-units was calculated from the intensities of the signals of the ethylenic protons in 1,2-units (5 ppm; 5.4–5.6 ppm) and in 1,4-units (5.4 ppm) (Table I). Three signals corresponding to different types of primary alcoholic groups were identified according to Fages and Pham.²⁵:



The OH-functionality (number of hydroxy per chain) was calculated from the integration of these

weak signals (requiring a large number of scans), knowing the molar mass (Table I).

Synthesis of HPBA

Hydrosilylation was used for grafting the aminoalkylsiloxane M_2A onto the 1,2-units of HPB. The reaction was carried out in hexane or toluene in the presence of a platinum catalyst: here again H_2PtCl_6 and Pt,DVDS were compared. IR absorption at 2120 cm^{-1} [$\text{Si}-\text{H}$ stretching in $\text{OSi}(\text{CH}_3)_2\text{H}$ groups] was used to follow the extent of the reaction as a function of time.

Speier's Catalyst. We found that long periods of induction were observed when the reactants and the catalyst were introduced together in the reactor. When the polymer was in excess with respect to the silane, the induction period may be completely suppressed if the polymer and the catalyst were left in contact for 15 min before adding the silane.¹⁴ This was interpreted by the necessary complexation of the double bonds of the polymer with platinum.

When polymer and silane were used in equimolar ratio, a time of contact of 15 min between polymer and catalyst markedly decreased the induction period, but the time-conversion plots still presented a phase of acceleration (Fig. 7). Simultaneously, the solution turned black and insoluble particles were observed under the microscope. These observations may be interpreted by the formation of very reactive colloidal $\text{Pt}(0)$ by reduction of $\text{Pt}(II)$ by the silane.²⁶ Effectively, the acceleration began sooner and was more pronounced when the concentration of silane was higher. A reaction scheme based on this assumption was in agreement with the observed kinetic behaviour.¹⁴

Karstedt's Catalyst. Contrary to H_2PtCl_6 , there was no induction period with Pt,DVDS (Figs. 8, 9) and a time of contact between polymer and catalyst did not change the initial rate (Fig. 12). This was consistent with the fact that $\text{Pt}(0)$ is already complexed by double bonds. If exchange between divinyltetramethyldisiloxane and HPB took place, the reaction was probably fast.

To compare the two catalysts, two cases should be distinguished. When the silane concentration was low (HPB in excess), there was no acceleration period in the case of H_2PtCl_6 and the time-conversion plots were similar in both cases. The comparison was favourable to H_2PtCl_6 : for a given Pt-concentration, the rates and the maximal yields were higher (Fig. 8). This means that, in these conditions, $\text{Pt}(0)$

Table I Macromolecular Characteristics of Commercial HPBs

	1,2-Units (%)	M_{nVPO}	M_{nSEC}	f_{OH}	OH ₁	OH ₂ (%)	OH ₃
HPB1	20	2800	2800	2.5	17	46	37
HPB2	20	3100	4300	2.6	15	49	36
HPB3	88.6	2000	1800	2.0	—	—	—

HPB1 and HPB2: polybd R45HT (Atochem); HPB3: G1000 (Nippon Soda).

filled by coordination with a double bond, regenerating the active intermediate (II).

The kinetic order in Pt was determined in a concentration range of $4.3 \cdot 10^{-4}$ – $1.5 \cdot 10^{-3}$ mol · L⁻¹ with a ratio [SiH]/[C=C] = 0.136. According to the second order in silane, plots of $1/[SiH] - 1/[SiH]_0$ versus time were linear during a large part of the reaction (Fig. 10). However, these straight lines did not pass through the origin and the intercept was more pronounced at high [Pt]₀. Moreover the slope of the linear part, k_{app} , increased with [Pt]₀ and a logarithmic plot of k_{app} versus [Pt]₀ led to an order in platinum equal to 1.25 (Fig. 11), whereas a value equal to 1 was derived for H₂PtCl₆ in similar conditions. This suggested some state of aggregation. On the other hand, the transient phenomenon observed in the plots of $1/[SiH] - 1/[SiH]_0$ versus time suggested some change in the reactivity of the catalyst. This was consistent with the hypothesis that a very active colloidal platinum was formed in the presence of silane functions.²⁶

When the reactants were used in equimolar ratio, using higher silane concentration, the comparison between the two catalysts was more difficult, because an acceleration took place in the case of H₂PtCl₆ (Fig. 12). At high Pt concentration ($\approx 10^{-3}$ mol · L⁻¹), the initial rates and the half-reaction times were shorter in the case of Pt,DVDS but both catalysts led to the same final yield (about 90%). It is worthwhile to note that the maximal rate obtained with H₂PtCl₆ at the inflexion point of the time-conversion plot was comparable to the initial rate in the case of Pt,DVDS. This may indicate that the active species formed in both cases were similar, probably a colloidal Pt(0) as suggested above. As usual in heterogeneous catalysis, the reactivity may largely depend on the particle size and state of aggregation. However if the Pt concentration is lowered ($\approx 3.0 \cdot 10^{-4}$ mol · L⁻¹), a limiting yield of about 70% is observed in the case of Pt,DVDS whereas H₂PtCl₆ leads slowly to 90% hydrosilylation. The explanation may be the same as in the previous section concerning the reaction of allylamine with

M₂. The inhibitory effect of tertiary amine is probably also effective in the case of a Pt(0) derivative. Thus in the present system, Pt,DVDS presented no advantage with respect to H₂PtCl₆.

Other Aminoalkylsiloxanes. The nature of the amino group and the length of the siloxane arm were varied in order to check the influence of the chemical structure of the QAS on the biocidal properties of the polymer.²⁷ 1-(*N,N*-dibutylaminopropyl) 1,1,3,3-tetramethyldisiloxane and 1-(*N,N*-dimethylaminopropyl) 1,1,3,3,5,5,7,7-octamethyltetrasiloxane were also grafted on HPB1. Hydrosilylation yields were always higher than 90%.

Characterization of HPBA

The ¹H NMR spectrum of the modified polymer (HPBA) showed an almost complete disappearance of the signal attributed to the 1,2-units whereas the signal of the 1,4-units was still present [Fig. 6(b)]. Grafting of the aminoalkylsiloxane was confirmed

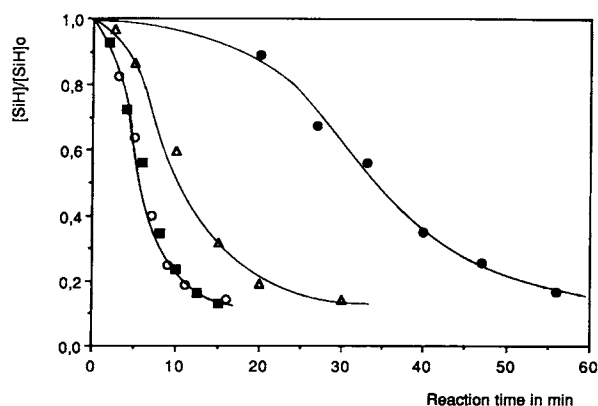


Figure 7 Induction period during the hydrosilylation of HPB by M₂A in the presence of H₂PtCl₆: influence of a time of contact (tc) between H₂PtCl₆ and HPB. [H₂PtCl₆] = $9.5 \cdot 10^{-4}$ mol · L⁻¹; [—CH=CH₂]₀ = [SiH]₀ = 0.33 mol · L⁻¹; temperature: 75°C. (●) tc = 0; (△) tc = 5 min; (■) tc = 15 min; (○) tc = 60 min.

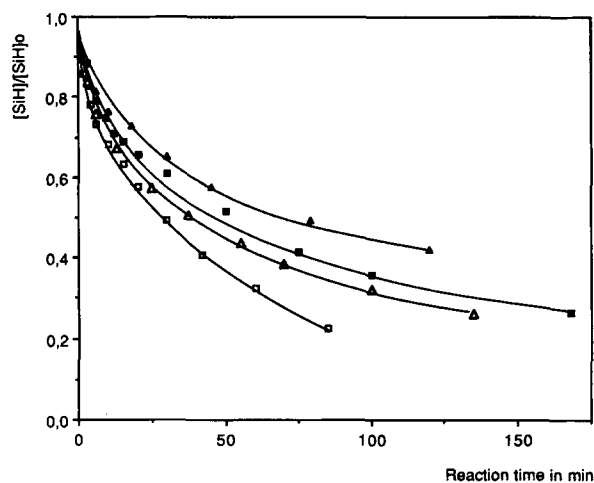


Figure 8 Catalytic activity of H_2PtCl_6 and Pt,DVDS on the kinetics of hydrosilylation of HPB by M_2A at a ratio $[-\text{CH}=\text{CH}_2]/[\text{SiH}] \gg 1$. $[-\text{CH}=\text{CH}_2]_0 = 0.66 \text{ mol} \cdot \text{L}^{-1}$; $[\text{SiH}]_0 = 0.086 \text{ mol} \cdot \text{L}^{-1}$; temperature: 75°C . H_2PtCl_6 ($t_c = 15 \text{ min}$): (■) $3.2 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$; (□) $8.0 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$. Pt,DVDS: (▲) $4.3 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$; (△) $7.8 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$.

by the presence of signals corresponding to CH_3 (0.05 ppm) and CH_2 (0.5 ppm) linked to silicon atoms.

We checked that the addition of the silane functions occurred mainly on the vinyl groups. The content of 1,4-units, x , after reaction may be calculated from the NMR spectrum of HPBA [Fig. 6(b)], considering the integrations of the protons in 1,4-

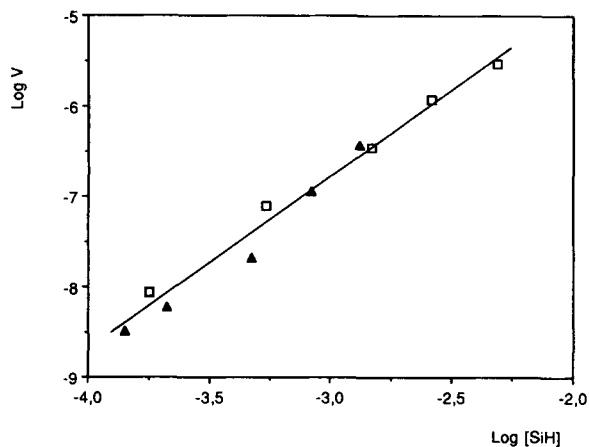


Figure 9 Determination of the kinetic order in silane in the presence of H_2PtCl_6 and Pt,DVDS at a ratio $[-\text{CH}=\text{CH}_2]/[\text{SiH}] \gg 1$. Temperature: 75°C . (□) $[\text{H}_2\text{PtCl}_6] = 9.7 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$; $[-\text{CH}=\text{CH}_2]_0 = 0.66 \text{ mol} \cdot \text{L}^{-1}$; $[\text{SiH}]_0 = 0.099 \text{ mol} \cdot \text{L}^{-1}$; (▲) $[\text{Pt,DVDS}] = 1.1 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$; $[-\text{CH}=\text{CH}_2]_0 = 0.66 \text{ mol} \cdot \text{L}^{-1}$; $[\text{SiH}]_0 = 0.09 \text{ mol} \cdot \text{L}^{-1}$.

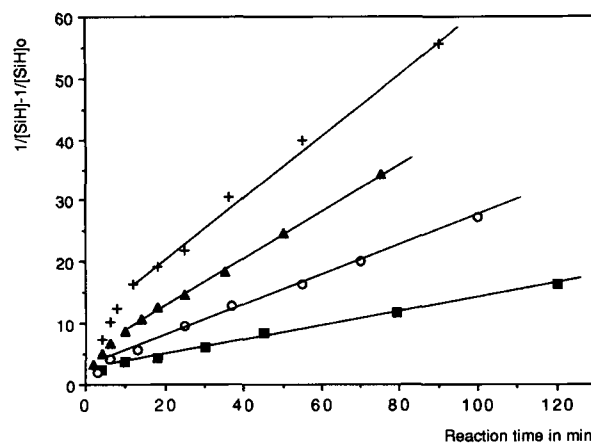


Figure 10 Second-order plots for the silane consumption during hydrosilylation of HPB with M_2A at a ratio $[-\text{CH}=\text{CH}_2]/[\text{SiH}] \gg 1$ in the presence of Pt,DVDS. $[\text{SiH}]_0 = 0.09 \text{ mol} \cdot \text{L}^{-1}$; $[-\text{CH}=\text{CH}_2] = 0.66 \text{ mol} \cdot \text{L}^{-1}$; temperature: 75°C . (■) $[\text{Pt,DVDS}] = 4.3 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$; (○) $[\text{Pt,DVDS}] = 7.82 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$; (▲) $[\text{Pt,DVDS}] = 1.1 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$; (+) $[\text{Pt,DVDS}] = 1.5 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$.

units, in unreacted 1,2-units, and in grafted 1,2-units. For HPB1, the value of x thus calculated was slightly but significantly lower than the theoretical value 0.8 ($x = 0.782 \pm 0.008$). Two explanations were considered:

1. First, disubstituted double bonds (1,4-units) might be weakly reactive in hydrosilylation. In this hypothesis, the fraction of reacted 1,4-units, deduced from the value of x , would be equal to 2.25%.
2. Second, the unreacted aminoalkylsiloxane

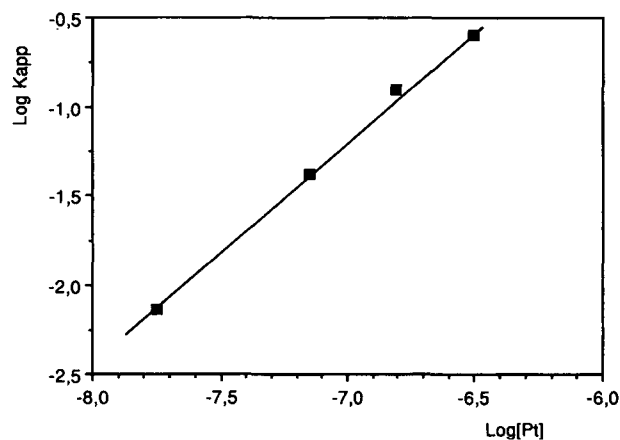


Figure 11 Kinetic order in Pt,DVDS during hydrosilylation of HPB with M_2A at a ratio $[-\text{CH}=\text{CH}_2]/[\text{SiH}] \gg 1$. $[\text{SiH}]_0 = 0.09 \text{ mol} \cdot \text{L}^{-1}$; $[-\text{CH}=\text{CH}_2] = 0.66 \text{ mol} \cdot \text{L}^{-1}$; temperature: 75°C .

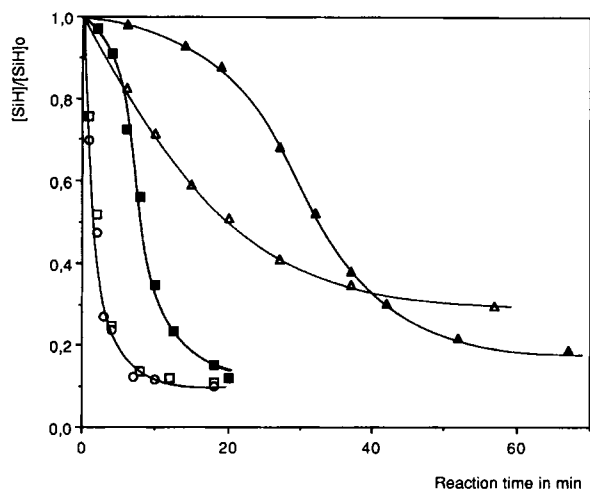


Figure 12 Catalytic activity of H_2PtCl_6 and Pt,DVDS on the kinetics of hydrosilylation of HPB by $\text{M}'_2\text{A}$ in equimolar ratio. $[\text{SiH}]_0 = [-\text{CH}=\text{CH}_2] = 0.33 \text{ mol}\cdot\text{L}^{-1}$; temperature: 75°C . (\blacktriangle) $[\text{H}_2\text{PtCl}_6] = 3.1 \cdot 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ ($t_c = 15 \text{ min}$); (\blacksquare) $[\text{H}_2\text{PtCl}_6] = 9.7 \cdot 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ ($t_c = 15 \text{ min}$). (\triangle) $[\text{Pt,DVDS}] = 2.9 \cdot 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ ($t_c = 0$); (\square) $[\text{Pt,DVDS}] = 9.7 \cdot 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ ($t_c = 0$); (\circ) $[\text{Pt,DVDS}] = 9.7 \cdot 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ ($t_c = 15 \text{ min}$).

might remain in the polymer in spite of methanol precipitation. In this case, x is equal to 0.8 and the contents of modified and unmodified 1,2-units may be calculated from the ^1H NMR spectrum. The values are 0.182 and 0.018, respectively (yield of hydrosilylation 91%). In this hypothesis, the content of free $\text{M}'_2\text{A}$ contained in the polymer was found equal to 0.022, a value corresponding closely to the content of unreacted 1,2-units (0.018). As the reactants were used in equimolar ratio in these experiments, this means that ungrafted $\text{M}'_2\text{A}$ was probably not eliminated by precipitation. This last hypothesis appeared more likely than the first one.

Molar Mass of HPBA

The experimental values of the molar masses of HPBA determined by SEC and VPO were always higher than the theoretical values (Table II). SEC

chromatograms were usually asymmetrical with a shoulder toward the higher molar masses (Fig. 13). An analysis of the SEC traces showed that the envelop could be resolved in two peaks, the peak of low molar mass corresponding approximately to the theoretical value, the other one corresponding to values 2–3 times larger. This was probably due to some chain coupling caused by the presence of M'_2 that acts as a bifunctional impurity (GC chromatograms of $\text{M}'_2\text{A}$ effectively showed the presence of residual M'_2 and the effect on molar mass was less pronounced when the purity of $\text{M}'_2\text{A}$ was improved). A similar phenomenon was observed by Cameron and Ourish²⁸ during hydrosilylation of polybutadiene by chlorodimethylsilane. In that case, hydrolysis of chlorodimethylsilane by traces of water was responsible for the formation of M'_2 .

OH-Functionality of HPBA

^1H NMR spectrum of HPBA showed three peaks between 3.1 and 4.1 ppm corresponding to the three types of primary alcohols previously discussed in the case of HPB. The functionality was calculated from the integrations of the signals and the theoretical molar mass of HPB. Values varying between 2.3 and 1.9 were found, that is, slightly lower than the initial value (2.5). This was probably due to a reaction of the OH groups with the silane. This was checked by mixing $\text{M}'_2\text{A}$ with an excess of isopropanol in the presence of hexachloroplatinic acid. 1-Dimethylaminopropyl 1-isopropoxy 1,1,3,3-tetra-methyl-disiloxane was formed quantitatively and identified by ^1H NMR [SiCH_3 , $\delta = 0.05$ and 0.09 ppm (s), 12H; SiCH_2 , $\delta = 0.5$ ppm (m), 4H; $(\text{CH}_3)_2\text{CH}$, $\delta = 1.2$ ppm (d), 6H; $\text{CH}_2-\text{CH}_2-\text{CH}_2$, $\delta = 1.5$ ppm (m), 2H; $\text{CH}_2-\text{N}(\text{CH}_3)_2$, $\delta = 2.2$ ppm (m), 8H; $(\text{CH}_3)_2\text{CH}$, $\delta = 4.1$ ppm (s), 1H].

The proportions of the three types of alcohols were modified after hydrosilylation (Table II). OH_1 was only slightly modified, but OH_2 strongly decreased and OH_3 increased. The apparent transformation of one type of hydroxy groups in another one was puzzling. This may be due to a migration of the double bond according to:

Table II Macromolecular Characteristics of Modified HPBs, HPBA

	Yield (%)	$M_{n\text{VPO}}$	$M_{n\text{SEC}}$	f_{OH}	OH_1	OH_2 (%)	OH_3
HPB1A	91	9800	10000	1.9	16	24	60
HPB2A	89	7700	9500	1.8	11	33	56
HPB3A	97	—	—	1.6	—	—	—

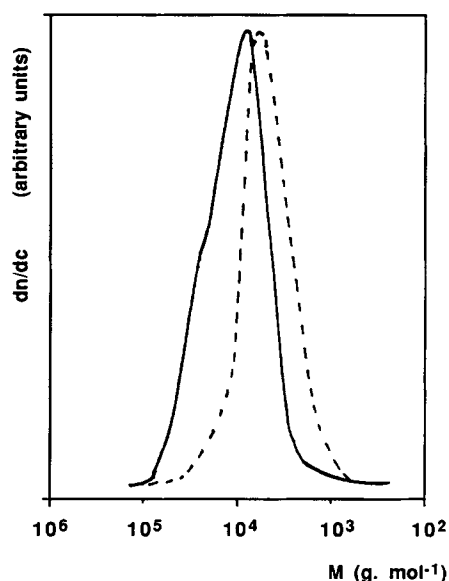
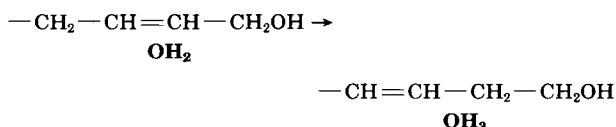


Figure 13 SEC traces of a sample of HPB2 ($M_n = 4300 \text{ g} \cdot \text{mol}^{-1}$, dashed line) and the same polymer grafted with 18% of *N,N*-dimethylaminopropyltetramethyldisiloxane ($M_n = 9500 \text{ g} \cdot \text{mol}^{-1}$, theoretical value: 7300).



Another explanation for an apparent increase of OH_3 might be the presence of traces of methanol used for polymer precipitation (the methyl protons of methanol have the same chemical shift as the methylene protons of OH_3). In this case, the functionality would be overestimated.

However, it is noteworthy that the limited loss of OH groups was more than compensated by the increase of the average DP of the polymer due to chain coupling. Thanks to this effect, the real functionality was largely higher than 2.

Quaternization of HPBA

Quaternization was carried out with alkyl bromides that are more reactive than chlorides. According to the literature, high yields are obtained in polar solvents such as ethanol or methanol.²⁹ However, HPBA is not soluble in these solvents, but it is soluble in a mixture of THF/ethanol (50/50). Attempts to carry out the reaction in this mixture were not satisfactory. In stoichiometric conditions, the yield of quaternization was limited to 60% (Fig. 14). An excess of alkyl bromide was necessary to get yields higher than 90%, but the excess of alkyl bro-

mid was very difficult to eliminate due to its high boiling point and to its solubility in the same solvents as the quaternized polymer (HPBAQ).

Experiments were also carried out in pure ethanol under reflux without an excess of alkyl bromide. The medium was heterogeneous at the beginning (Fig. 14). However, as the reaction is progressing, the polymer becomes gradually soluble. In these conditions, the reaction was almost complete in about 8 h whatever the alkyl bromide between $\text{C}_8\text{H}_{17}\text{Br}$ and $\text{C}_{16}\text{H}_{33}\text{Br}$.

^1H NMR spectrum of HPBAQ reported in Figure 6(c) showed that the signal at 2.18 ppm corresponding to the protons of the amino groups disappeared. New signals at 3.35 and 3.48 ppm were respectively assigned to the protons of CH_3N^+ and CH_2N^+ groups. These assignments were confirmed by the study of a model *bis*-(dimethyloctylpropylammonium) tetramethylsiloxane dibromide. The ^1H NMR spectrum of this compound showed two signals at 3.28 and 3.55 ppm with an integration ratio of 3 : 2. In the case of HPBAQ, the yields of quaternization deduced from NMR are higher than 90%, but the unreacted octyl bromide not separated from the polymer complicated the spectrum. A potentiometric titration of the bromide ions gave similar values.

SEC chromatograms of HPBAQ could not be obtained, probably because of retention on microstyragegel columns due to the ionic character of the polymer.

OH-Functionality of HPBAQ

The determination of the OH groups in HPBAQ by NMR was more difficult, because the alcoholic

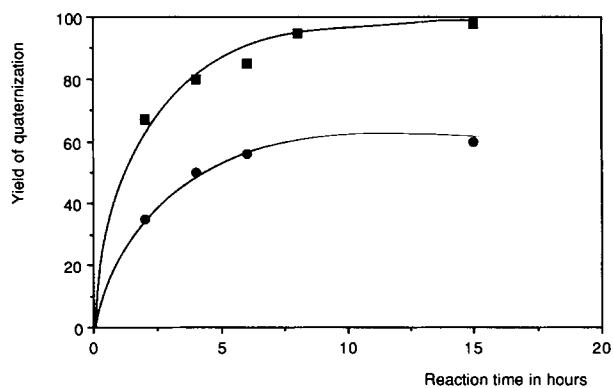


Figure 14 Quaternization of HPBA by $\text{C}_8\text{H}_{17}\text{Br}$ in equimolar ratio. $[\text{C}_8\text{H}_{17}\text{Br}] = 0.3 \text{ mol} \cdot \text{L}^{-1}$; (●) in a mixture of THF/ethanol (50/50) at reflux; (■) in pure ethanol ($T = 78^\circ\text{C}$).

groups OH₃ are hidden by the signals corresponding to the protons in the α position of the quaternary nitrogen atom. In the region around 4 ppm, the spectrum showed two peaks assigned as OH₁ and OH₂. Assuming that the proportions of the different types of alcoholic groups were not modified during the reaction, a value of 1.9 was calculated for the apparent functionality of HPB1AQ, identical to that of HPBA. There was no loss of hydroxy group during quaternization.

CONCLUSION

Conditions were found for the preparation of HPBs bearing covalently bound QAS as lateral groups through a disiloxane spacer. The yields reach 90% for each step. A close examination of the side reactions showed that they were minimal and globally not detrimental. A small decrease of the number of OH groups per chain was observed during hydrosilylation but the functionality was artificially maintained at values higher than 2 by some chain coupling due to traces of tetramethyldisiloxane M₂.

Several polymers were prepared containing various proportions of QAS and various substituents on the nitrogen atom. These polymers were used to prepare polyurethane films and the biocidal properties of the coatings were assessed in various conditions.^{27,30}

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