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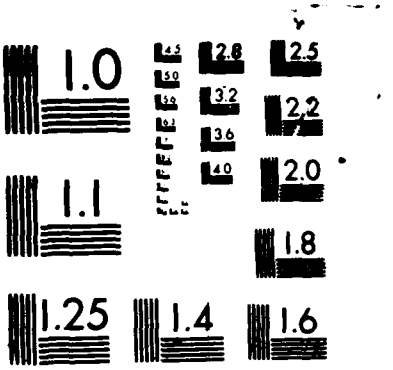

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NEW SYNTHETIC ROUTES TO POLYSILANES

by

K. Matyjaszewski, Y. L. Chen and H. K. Kim

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New Synthetic Routes to Polysilanes

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Three new synthetic routes for the synthesis of polysilanes have been applied: low temperature coupling in the presence of ultrasound, modification of poly(alkylarylsilylene) with triflic acid, and ring-opening polymerization. Low temperature reductive coupling of dichlorosilanes with sodium in the presence of ultrasound leads to monomodal polymers with low polydispersity ($\overline{M}_w/\overline{M}_n$=1.2) in contrast to bimodal polymers prepared by the thermal coupling. Modification of polysilanes with triflic acid gives access to new polysilanes with pendant alkoxy or amino substituents. Ring-opening polymerization have been successful only for the strained cyclic polysilanes with small substituents.

A rapidly increasing number of publications on polysilanes documents current interest in these polymers (1). Polysilanes are potentially applicable in microlithography as high resolution UV-resists (2), imageable etch barriers (3), or contrast enhancement layers (4). They have been successfully used as precursors to Si-C fibers (5) and ceramic reinforcing agents (6). Polysilanes have also initiated polymerization of vinyl monomers (7). Doping of polysilanes have increased their conductivity to the level of semiconductors (8). Very recently polysilanes were used as photoconductors (9) and non-linear optical materials (10).

At present, the only synthetic method leading to high molecular weight polysilanes is based on the Wurtz condensation reaction between dichlorodisubstituted silanes and alkali metals (low molecular weight oligomers were also prepared by dehydrogenation of secondary organosilanes). This reaction often gives a low yield of the desired linear high molecular weight polymer. Low molecular weight linear and cyclic oligomers in addition to the insoluble gel are the major side products. Target high molecular weight polysilane often has a very broad molecular weight distribution which limits its application in high resolution microlithography. Some improvements in the properties of the polymer and the yields were recently reported(11,12). Addition of

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different solvents as well as reverse addition of alkali metal dispersions were reported. Nevertheless the desired product was rarely formed in yields higher than 50% and bimodality of molecular weight distribution remained. The high molecular weight polymer could be separated by fractional precipitation but it still has a high polydispersity.

We have been recently studying new pathways leading to polysilanes with low polydispersity and controlled structures. Our research is focused on three areas. The first one is low temperature reductive coupling in the presence of ultrasound. This leads to monomodal polymers with molecular weights in the range from $\overline{M}_n$=50,000 to $\overline{M}_n$=300,000 and polydispersities as low as $\overline{M}_w/\overline{M}_n$=1.20 (in addition to usually formed cyclic oligomers).

The second approach to linear polysilanes is based on the modification of polysilanes prepared by the reductive coupling method. The severe conditions of this reaction allow only alkyl or aryl substituents at the silicon atom in the starting dichlorosilane. Therefore only alkyl or aryl substituted polysilanes are known. We have successfully prepared new polysilanes with pendant alkoxy and amino side groups. This approach allows fine tuning of the properties of polysilanes.

The third synthetic pathway leading to polysilanes employs the ring-opening polymerization of strained cyclic polysilanes. The target is the preparation of polysilanes with active end groups which will be capable of reacting with other monomers leading to block and graft copolymers.

Experimental

Phenylmethyldichlorosilane (Petrarch) was distilled prior to use and dried over CaH_2. Toluene was distilled from CaH_2 and dried over CaH_2. The known amounts of sodium were placed in a flask filled with toluene and purged with dry argon. This flask was placed in the ultrasonic bath (75-1970 Ultramet II Sonic Cleaner, Buehler Ltd.) until stable dispersion of sodium was formed. In some experiments an immersion-type ultrasonic probe was used (W-140, Heat Systems-Ultrasonics, Inc.). A toluene solution of dichlorosilane was added to the reaction flask in a controlled manner under inert gas. The reaction was quenched after the required time by using equimolar mixtures of water and ethanol. The organic phase was later added to a large excess of isopropanol leading to the precipitation of the polymer. The polymer was dried and the yield determined gravimetrically. Molecular weights and polydispersities were determined by gpc using polystyrene standards. The compositions of the polymers were measured by NMR. The filtrate remaining after the evaporation of the isopropanol was analysed by gc/ms, gpc and hplc.

All other reactions were carried out under dry inert gas (nitrogen or argon). Reagents were distilled before use. Octaphenylcyclotetrasilane (mp=322 ^{0}C) was prepared from diphenyldichlorosilane and Li in 27% yield.

NMR spectra were recorded on 300 MHz (GE) or 80 MHz (IBM) spectrometers. UV spectra were recorded using a 9420 IBM spectrometer. GPC analysis was performed using Waters systems 10^6, 10^5, 10^4 10^3 (or linear ultrastyragel) and 500Å Waters columns. Molecular weights are

based on the narrow polystyrene standards (actual molecular weights (VPO) are approximately two times higher).

Results and Discussion

Low Temperature Coupling in the Presence of Ultrasound.

The coupling of dichlorosilanes with sodium was previously studied in boiling toluene. Under these conditions (above the melting point of sodium) the surface of sodium was continuously reactivated by rapid stirring. This reaction has not yet been described at lower temperatures. There is a little information on the mechanism of the coupling reaction. Formation of high polymer at relatively low conversion suggests the chain growth mechanism and not the step growth mechanism which is usually observed for the condensation process. Thus, undoubtedly some active species should be present at the chain ends. Silyl radicals, radical anions and silylenes were proposed as the hypothetical active species (1,12). The effect of addition of the triethylsilane (trap of silylene) is similar to the effect of the inert hexane (11). Addition of diglyme which is used as an agent stabilizing anions by solvation of counterions considerably reduced the degree of polymerization although it increased the final yield of the polymer. Thus, silyl radicals are the most probable chain carriers.

The first step in the polymerization is the electron transfer from sodium to dichlorosilane and the formation of the corresponding radical anion. The latter upon elimination of the chloride anion is transformed to the silyl radical. To fit the chain growth mechanism, the reactivities of the macromolecular radicals must be higher than the reactivities of the monomeric radicals. The latter after electron transfer and elimination of chloride anion could be transformed to the reactive silylenes. Thus, in principle, two or more mechanisms of chain growth are possible:

$$Cl_2SiR^1R^2 + Na \rightarrow [Cl_2SiR^1R^2]^{\cdot -} \rightarrow [ClSiR^1R^2]^{\cdot} + Na^+ \rightarrow \rightarrow \text{"propagation 1"}$$

$$\downarrow Na \qquad (1)$$

$$[ClSiR^1R^2]^- + Na^+ \rightarrow SiR^1R^2{:} + NaCl$$

$$\downarrow \qquad\qquad \downarrow$$

$$\text{"propagation 2"} \qquad \text{"propagation 3"}$$

This can result in polymodality of the molecular weight distribution when the exchange between the chain carriers is slow and they lead to the independent growth. Polymodality of the MWD is observed indeed. This phenomenon has been explained by differences in diffusion of the short and long polymer chains, but multiplicity of the chain carriers seems to us to be a more probable explanation.

The origin of the reaction which limits the chain growth is not known. Probability of cyclization, one of the side reactions, should decrease strongly with the polymerization degree in agreement with the

Jacobson-Stockmayer theory (13). Usually transfer and termination reactions in polymerization have energies of activation higher than propagation. Thus, we attempted coupling reactions at temperatures lower than usually applied. In order to assure the access of dichlorosilane to the surface of the sodium, the dispersion was continuously regenerated by ultrasonication. The results of these preliminary studies are shown in Table 1.

We have observed a dependence of the yield, polymerization degree, and polydispersity of polysilanes on temperature and also on the power of ultrasonication. In the ultrasonication bath the simplest test of the efficiency of cavitation is the stability of the formed dispersion. It must be remembered that the ultrasonic energy received in the reaction flask placed in the bath depends on the position of the flask in the bath (it is not the same in each bath), on the level of liquid in the bath, on temperature, on the amount of solvent, etc. When an immersion probe is used the cavitation depends on the level of the meniscus in the flask as well. The power is usually adjusted close to 50% of the output level but it varies with the reaction volume, flask shape, and other rection conditions. The immersion-type probe is especially convenient at lower temperatures.

GPC traces of poly(phenylmethylsilylenes) prepared in the ultrasonication bath are shown in Fig. 1. In contrast to thermal condensation, monomodal high molecular weight polymer is formed. Oligomeric cycles (mostly cyclic pentamer), formed usually in high yield (cf. Table 1), can be very easily separated from the reaction mixture by precipitation with isopropanol. The molecular weight of polysilanes decreases and polydispersity increases with temperature.

The coupling reaction is usually rapid and completed in a short time after the addition of dichlorosilane. Ultrasonication accelerates the recovery of the sodium surface and enables large momentary excess of sodium to chlorosilanes. We have, however, observed a change in the molecular weight and polydispersity at longer reaction times. This is illustrated in Fig. 2.

Because the coupling reaction is usually carried out in excess sodium ($[Na]_0/[Si\text{-}Cl]_0=1.2$), degradation of the polymer is possible. We had prepared polysilanes and tested this possibility by their reaction with and without sodium in the presence of ultrasonication. Monomodal and bimodal polysilane was used. Reaction without sodium led to random degradation whereas ultrasonication with sodium favored degradation of the low molecular weight polymer. Thus, the monomodality of polysilanes obtained by ultrasonication can have its origin in the selective and more rapid degradation of the low molecular weight polymer, which might have a different microstructure than the high polymer, and may also favor the formation of the high polymer by reaction conditions different than those in a typical thermal process. If two independent mechanisms of chain growth are assumed, a lower temperature will favor the process proceeding with the lower activation energy (high polymer). If polymodality has its origin in diffusion phenomena, cavitation can eliminate the formation of low oligomers. Eventually, a large excess of sodium may also influence the kinetics of coupling and favor the formation of high polymer.

The degradation of polysilanes in the presence of sodium indicates that the polymer is a kinetic product and is easily degraded to

thermodynamically more stable cyclic oligomers. Thus, some earlier experiments performed with soluble initiators (biphenyl radical anion) (11) in which only oligomers were formed may indicate very rapid polymerization as well as very rapid degradation. This means that isolation of the high polymer could have been possible but at shorter reaction times. We believe that the reproducibility of our results will enable more systematic kinetic and mechanistic studies of the reductive coupling of dichlorosilanes leading to the formation of high polymers.

Modification of Polysilanes

The presence of alkali metal during reductive coupling practically prevents the synthesis of polysilanes with groups which can be easily cleaved under basic conditions, such as pendant alkoxy or amino substituents. Polysilanes with pendant functional groups are not known. We have recently discoverd a very efficient method of functionalization of polysilanes.

Model reactions show that methyl, chloro, and aryl groups can be rapidly and quantitatively displaced by triluoromethanesulfonic acid:

$$R\text{-}Si(CH_3)_2\text{-}Si(CH_3)_2\text{-}R + 2HOSO_2CF_3 \rightarrow \underset{+2RH}{CF_3SO_2O\text{-}Si(CH_3)_2\text{-}Si(CH_3)_2\text{-}OSO_2CF_3}$$

where $R=C_6H_5$, CH_3, Cl (2)

Bis 1,2-(trifluoromethanesulfonlyloxy)tetramethyldisilane is a stable and reactive compound towards different nucleophiles (14). It reacts rapidly with pyridine forming mono and (at a 1:2 ratio) disalts with pyridine. With secondary amines this compound forms the corresponding disilyldiamine. Dialkoxydisilanes were prepared in good yields in the reaction with different alcohols:

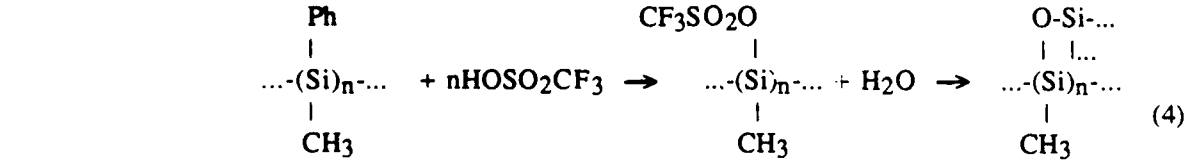
$$CF_3SO_2O\text{-}Si(CH_3)_2\text{-}Si(CH_3)_2\text{-}OSO_2CF_3 + 2ROH \xrightarrow[-BH]{B:} RO\text{-}Si(CH_3)_2\text{-}Si(CH_3)_2\text{-}OR$$

(3)

where RO-: CH_3O-, CF_3CH_2O-, $CH_2=CHCH_2O$-, $(CH_3)_3CO$-, etc

We used a similar reaction for the modification of polysilanes. Poly(phenylmethylsilylene) has been chosen as the model polysilane because cleavage of the aryl groups is much faster than that of the alkyl groups. The displacement reaction proceeds very rapidly at room temperature and immediately after addition of the acid the sharp signal of the benzene is found. ^{1}H-NMR spectra of the initial polymer indicate the presence of different iso-, syndio-, and atactic structures. The chemical shifts of the methyl groups after displacement of the phenyl groups by triflate groups move downfield approximately 1.2 ppm (cf. Fig. 3). A similar chemical shift of methyl groups is observed for mono and disilanes with triflate groups.

Polysilanes bearing triflate groups are very reactive and form an insoluble gel with a trace of moisture. The triflate group is hydrolized to silanol which rapidly condenses with the remaining triflate groups to a siloxane unit, linking intra or intermolecularly silicon atoms:



(4)

Polymers with triflate groups react with alcohols to form alkoxysubstituted polysilanes. This reaction occurs readily in the presence of bases. The best results were obtained using triethylamine and hindered pyridine. In Fig. 3c the NMR spectrum of the reaction mixture containing the excess of triethylamine is shown, the methyl groups from the polymer chains absorb in the range typical for alkoxysilanes. Reaction in the presence of unsubstituted pyridine leads to the formation of insoluble polymer probably by attack at the p-C atom in the silylated pyridine.

Polysilanes with alkoxy groups are more light sensitive than conventional polysilanes. They degrade rapidly in the presence of light in agreement with the facile formation of silylene from dialkoxydisilanes. Properties of these polymers are currently being investigated.

Ring-Opening Polymerization

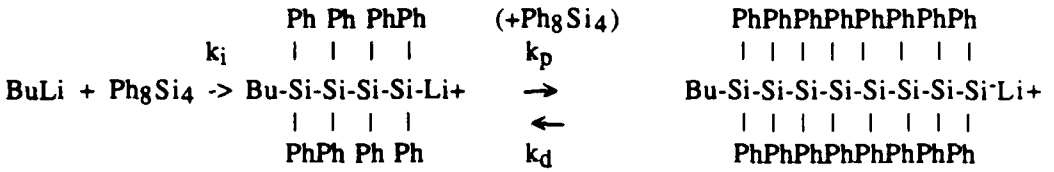
The formation of the linear polymer from the cyclic monomer requires a decrease of the free energy. Because usually entropy is lost during polymerization, the main driving force for the ring-opening process is the release of the angular strain upon conversion of the cycles to linear macromolecules. Thus, a majority of three- and four-membered rings can be readily and quantitatively converted into polymers.

Nonpolymerizability may have its origin either in thermodynamics or in kinetics. Some monomers, in spite of the strain, cannot be homopolymerized but readily copolymerize. 1-Benzyl-2,2-dimethylaziridine or tetramethyloxirane can serve as the examples (15). On the other hand unsuccessful polymerization can be ascribed to the lack of the initiator which could lead to the formation of active species capable of a significant decrease of the energy barrier for propagation. Therefore oxetanes, thietanes, azetidines, and aziridines cannot be polymerized by an anionic but only by a cationic mechanism(16).

Quite often in the ring-opening polymerization, the polymer is only the kinetic product and later is transformed to thermodynamically stable cycles. The cationic polymerization of ethylene oxide leads to a mixture of poly(ethylene oxide) and 1,4-dioxane. In the presence of a cationic initiator poly(ethylene oxide) can be almost quantitatively transformed to this cyclic dimer. On the other hand, anionic polymerization is not accompanied by cyclization due to the lower affinity of the alkoxide anion towards linear ethers; only strained (and more electrophilic) monomers can react with the anion.

We have attempted the polymerization of octaphenylcyclotetrasilane, which is the only commercially available strained cyclopolysilane.

We have used different anionic, cationic, and metathesis initiators but after the reaction of the initiator with one monomer molecule (initiation, k_i) no subsequent propagation was observed:



(5)

This may suggest that either propagation is very slow due to the low reactivity of the derived species or that the equilibrium constant $K=k_p/k_d$ is very low which means that the cyclic tetramer is more stable than the polymer chain. This is apparently in agreement with the high yield (up to 40%) of cyclic tetramer; the yield of the polymer in the classical Kipping experiment of the coupling of diphenyldichlorosilane had to be very low because in addition to cyclic tetramer, large quantities of cyclic pentamer and hexamer were formed. Only very recently was existance of polysilanes with two aryl substituents proved by Miller who prepared soluble diaryl polysilanes with long p-alkyl substituents (17). Yields and stabilities of these polymers were not reported.

The interactions between bulky phenyl substituents in the polymer chain can give more steric hindrance than the deformation of the valency angles in the four membered ring. Similar interactions prevent the polymerization of 1,1-diphenylethylene and 2,2-diphenyloxirane (16). Thus, octaphenylcyclotetrasilane can be thermodynamically more stable than linear perphenylpolysilane and no initiator exists capable of converting this cycle to the linear polymer.

On the other hand, anions formed by the ring cleavage of octaphenylcyclotetrasilane may be very unreactive due to steric hindrances as well as to the formation of the tight silyl ion pair with alkali metals. We have attempted to decrease these interactions by using cryptands in order to better solvate the alkali metals and form the loose, separated ion pair. However, in addition to the rapid cleavage of one ring no propagation was observed. Using a 10 fold excess of monomer to butyl lithium in the presence of cryptand [2.1.1], only 10% of the monomer was converted to the linear chain; the rest did not react even after a longer time or at higher temperatures.

The polymerizabilty of cycles should increase for rings with smaller substituents. It has been reported that substitution of the chlorine atoms by alkyl groups in octachlorotetracyclosilane using methyl lithium led to the ring cleavage, indicating the possibility of polymerization. The sensitivity towards cationic or anionic systems should strongly depend on the structure of the substituents. Alkoxy groups may strongly stabilize positive charge and in a way similar to vinyl ethers can facilitate cationic polymerization. On the other hand, cyano groups should favor the anionic process. The facile displacement of phenyl groups by triflic acid was used as the first step in the synthesis of the four-membered cycles with alkoxy and cyano groups. During this substitution different isomers were formed and at the ratio 3:1 ($[HOSO_2CF_3]_0$:$[Ph_8Si_4]_0$) seventeen signals of methoxy groups were

observed by ^1H NMR. The presence of different isomers in the puckered four-membered ring indicates small differences in reactivities of different aryl groups. The excess of the acid was observed by NMR at a ratio higher than 4:1 which showed difficulty in the formation of the geminal ditriflate. In the preliminary experiments, the ring-opening polymerization of octamethoxycyclotetrasilane led to a polymer with molecular weight $\bar{M}_n=10^4$ and high polydispersity. The conditions leading to better defined polymers are at present being investigated.

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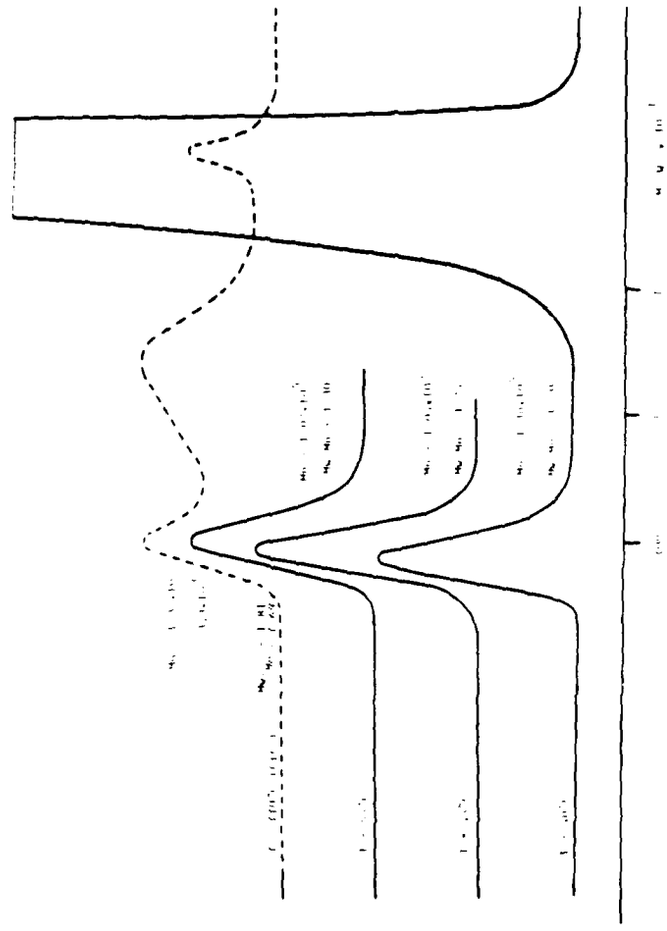
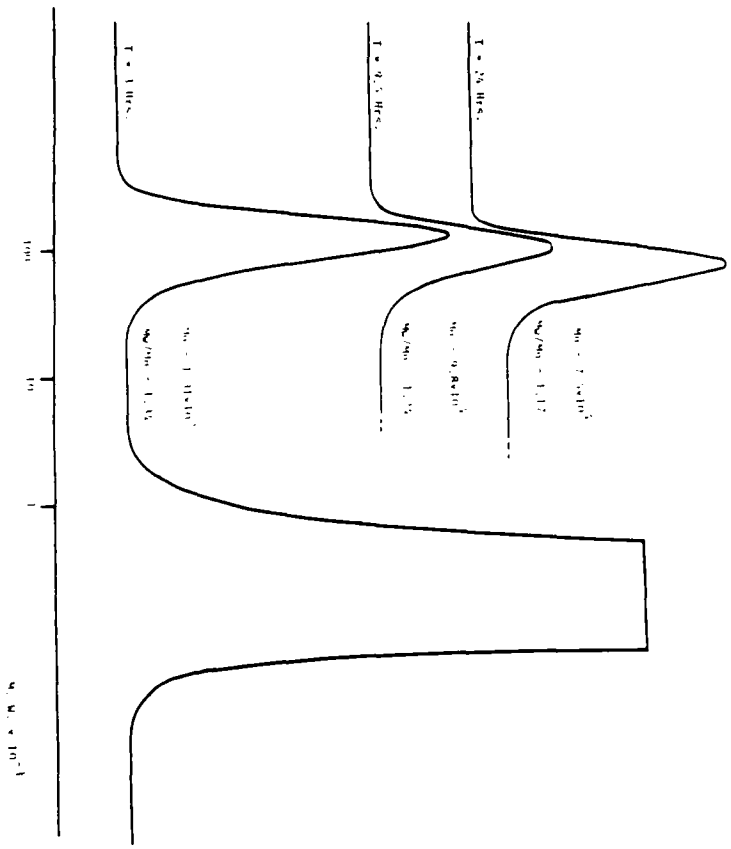
Captions for Figures

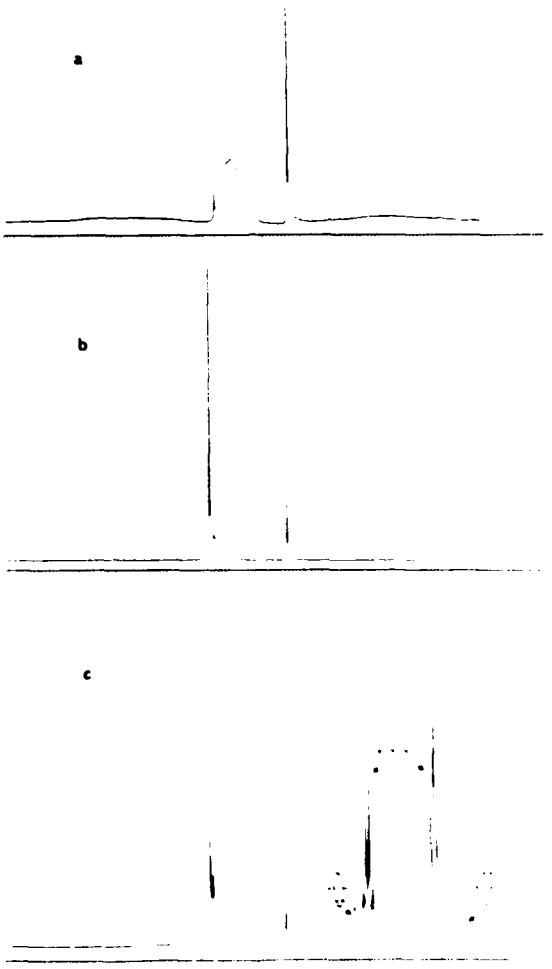
Fig. 1. GPC traces of the polymerization mixtures of phenylmethyldichlorosilane ($[M]_0$= 0.32 mol/L) and sodium ($[Na]_0$= 0.7 mol/L) in toluene after 6 hours and quenching with dry ethanol. Reaction temperatures : 55, 45, and 40^0 C.

Fig. 2. GPC traces of the same polymerization mixtures as in Fig. 1 at 55^0 C quenched after 3, 9.5, and 24 hours.

Fig. 3. ^{1}H-NMR spectra of poly(phenylmethylsilylene) ($[(SiPhMe)n]_0$=0.42 mol/L) (a), after reaction with triflic acid ($[CF_3SO_3H]_0$= 0.34 mol/L (b), and poly(methylmethoxysilylene) ($[(SiOMeMe)_n]_0$= 0.42 mol/L) (c) in $CDCl_3$ using CH_2Cl_2 as internal standard.



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